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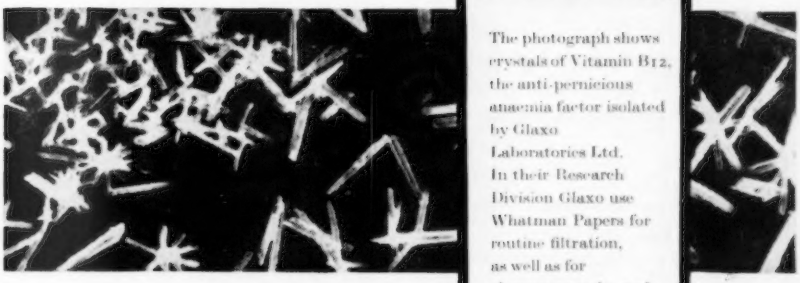

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# Incidental information

No.13

*Items of interest from our laboratory notebooks*

▶ Most analysts know about 1:10-phenanthroline and many use it for iron determinations. Not so many people seem to know that **4:7-diphenyl-1:10-phenanthroline** is twice as sensitive as 1:10-phenanthroline in the colorimetric determination of iron. There are several papers on the subject but the latest is *Analyst*, 1958, **83**, 80. The reagent is also called **Bathophenanthroline**, and we make it.

▶ Then, again the substitution of methyl groups in the 2:9 positions has the interesting effect of making the reagent insensitive to iron and we then have a selective and sensitive reagent for copper (see *Anal. Chem.*, 1956, **28**, 1158). Hopkin & Williams make **2:9-dimethyl-1:10-phenanthroline** (sometimes called **Neocuproin**).

▶ One does not think of sulphate as a radical one can determine absorptiometrically, but this is now possible for low concentrations. **Barium chloranilate** is the reagent and there are two papers on the subject—*Anal. Chem.*, 1957, **29**, 281 and *Anal. Chem.*, 1958, **30**, 202. Hopkin & Williams make it.

▶ Hopkin & Williams Ltd. were also early off the mark with supplies of the remarkable new colour-producing reagent for fluoride ions, **3-aminomethylalizarin-NN-diacetic acid**, described by Belcher, Leonard and West (*Talanta*, 1959, **2**, 92.) This important reagent is already available from stock.

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# ANALYTICAL ABSTRACTS

## 1.—GENERAL ANALYTICAL CHEMISTRY

*General reviews of progress, reagents and methods of general application.*

4655. **Requirements for analysis by differential migration.** H. H. Strain (Argonne National Lab., Lemont, Ill., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 818–821.—The important features common to all differential migration methods of analysis are reviewed and modifications and applications discussed. K. A. PROCTOR

4656. **Diffusion analysis of ions in gels.** M. Antelman, D. Eby and G. B. Kauffman (Hampshire Chemical Corp., Nashua, N.H., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 829–833.—Mixtures of common ions in 0·1 *N* soln. are partly resolved by radial differential diffusion in gels by means of chemical potential gradients. The gels are thick and made of gelatin, poly(vinyl alcohol), or Na alginate. The method is well suited to qual. analysis. For quant. determinations place 0·05 ml (as a round drop) on the central circle of the gel plate, measure the radial distance traversed after known time-intervals, and compare with a calibration curve of distance *vs.* log concn. (Fick's law). For colourless ions use a developer. Thus $Pb(NO_3)_2$ (0·1 to 10 *N*) is determined (no details given) to within ± 0·7%, with KI to arrest diffusion. For a series of halides it is shown that the diffusion of the anion is affected by the cation (Na, K or $NH_4^+$) present, though ions diffuse, and can be determined, independently. Interaction between ions and the gel may also cause interference. J. P. STERN

4657. **Use of amalgams in chemical analysis.** J. Doležal, B. Moldan and J. Zýka (Dept. Anal. Chem., Charles' Univ., Prague). *Chem. Listy*, 1958, **53** (4), 398–408.—A detailed survey of the properties and use of amalgams in the reduction and determination of numerous elements is given. (81 references.) J. ZÝKA

4658. **Schiff reagent of calibrated sensitivity.** H. Elftman (Columbia Univ., New York). *J. Histochem. Cytochem.*, 1959, **7**, 93–97.—The sensitivity of Schiff's reagent for the detection of low concn. of aldehyde increases as the concn. of $H_2SO_3$ in the reagent is decreased. The calibration of the sensitivity is readily accomplished by titration against iodine (Lugol's soln.). The stability of Schiff's soln. depends on decreasing the evaporation of $SO_2$ and on retarding the change of sulphite to sulphate; to this end, refrigeration of a soln. containing more $SO_2$ than will be required, followed by evacuation of the excess of $SO_2$ or the use of chemical preservatives (*e.g.*, 0·5% of quinol), are proposed. Spectrophotometric measurements of the coloured soln. produced by adding aldehyde to Schiff's reagent indicates that at least two compounds may result; one has a violet colour but, when the concn. of aldehyde is so low that only a Schiff's reagent of low sulphurous titre will react with it, a red colour is produced; spectrophotometric analysis shows this to be different from the original basic fuchsine and validates its use as an end-point indicator in the reaction of aldehyde with Schiff's reagent. K. R. C.

4659. **Thiomalic [mercaptosuccinic] acid in inorganic analysis.** R. N. Sen Sarma (Jadavpur Univ., Calcutta). *Sci. & Cult.*, 1958, **23** (8), 434–435.—Preliminary investigations indicate that mercaptosuccinic acid (**I**) may be used as a standard reducing agent in volumetric analysis, and $Fe^{3+}$, $Cu^{2+}$, $Mn^{7+}$, $Cr^{6+}$ and $V^{5+}$ have been quant. determined by direct titration with an aq. soln. of **I** in weakly acid medium. **I** may be also be used as a colour-forming reagent, stable coloured products being formed with $Fe^{3+}$, $Ni^{2+}$, $Co^{2+}$, $U^{6+}$ and $Mo^{6+}$. Iron, Mn, Pb, Bi, Hg and $UO_2^{2+}$ are not pptd. with aq. $NH_3$ in the presence of an excess of **I**, which enables the rare-earth elements to be separated from them. Determination of $Cu^{2+}$, Fe, $Mn^{2+}$ and $Ni^{2+}$ can be made by a complexometric titration of the coloured products formed with **I**; the coloured system with Fe may be used as an indicator in the titration of Ca, Mg and Pb with EDTA. The use of **I** as a pptg. agent is discussed: $Hg^{I}$ forms a black ppt., and $Pb^{II}$, $Hg^{II}$, Zn, Cd, $Sn^{II}$, Ag and $W^{VI}$ form white ppt. in weakly acid soln. K. R. C.

4660. **Polarographic examination of the chelating power of EDTA and some closely related chelating agents.** W. Hoyle and T. S. West (Chem. Dept., Univ., Birmingham, England). *Talanta*, 1959, **2** (2), 158–164.—A rapid polarographic method is described for studying the stability of new complexones, in which a standard curve relates the half-wave potentials to the stability constants of a group of metal chelates. The selection of a suitable cation is discussed, and it is shown that only $Cu^{II}$ and Cd, among common cations, are suitable, Cu being more satisfactory than Cd. From a study of the polarograms of a number of cupric chelates recorded at pH 2·5 and room temp., the chelate of di-(2-hydroxyethyl)glycine (DHEG), with $E_{\frac{1}{2}} = -0{\cdot}02$ and $\log_{10}K = 8{\cdot}1$, is chosen as zero reference standard, and a curve of $\Delta \log_{10}K$ *vs.* $\Delta E_{\frac{1}{2}}$ (where $\Delta$ is the difference between the chelate and DHEG values) is constructed, stability constants being taken from the literature. Values of $E_{\frac{1}{2}}$ are tabulated for 18 chelating agents, and $\log_{10}K$ values for 6 of these obtained from the curve. The curve appears to be linear for the known complexones, but this may not hold for newer reagents which are much more powerful in cation-binding power. The polarographic technique is described, and it is claimed that data on the chelating power of new reagents can be obtained in a few hours by the present method, compared with days by conventional methods. R. E. ESSERY

4661. **Complexones. XXX. Diethylenetriamine-penta-acetic acid (DTPA).** G. Anderegg, P. Nägeli and G. Schwarzenbach (Lab. f. anorg. Chem., Eidg. Tech. Hochsch., Zurich, Switzerland). *Helv.*

*Chim. Acta*, 1959, **42** (3), 827–836 (in German).—DTPA with metal cations $M^{n+}$ forms complexes of the type $MZ^{n-5}$, $MHZ^{n-4}$ and $M_2Z^{2n-5}$ where $Z^{5-}$ stands for the anion of DTPA. Bimetallic complexes of type $MM'Z^{n_1+n_2-5}$ are also formed. The stability constants of these species with Ca, Mn, $Fe^{II}$, $Fe^{III}$, Co, Ni, Cu, Zn, Cd, Pb, Hg and Ce were determined by using 7 methods. The DTPA complexes are considerably more stable than the corresponding EDTA complexes, making DTPA a better titrant in complexometry. G. P. COOK

4662. **Analytical applications of the complexones. XV. 1:2-Diaminocyclohexanetetra-acetic acid as an analytical reagent.** F. Bermejo Martínez and R. Rey Mendoza (Lab. de Quím. Anal. de la Fac. de Ciencias, Santiago de Compostela, Spain). *Inf. Quím. Anal.*, 1959, **13** (2), 31–37.—The apparent oxidation potential of 1:2-diaminocyclohexanetetra-acetic acid is a linear function of the pH of the soln. The reagent is not attacked by $K_2Cr_2O_7$, $KBrO_3$, iodine or $H_2O_2$ in acid soln. at room temp., but $KMnO_4$ and $Ce(SO_4)_2$ react under these conditions, as does iodine in alkaline soln.
G. H. FOXLEY

4663. **Principles of end-point detection in chelometric titrations using metallochromic indicators. Characterisation of end-point sharpness.** C. N. Reilley and R. W. Schmid (Univ. of N. Carolina, Chapel Hill, U.S.A.). *Anal. Chem.*, 1959, **31** (5), 887–897.—A numerical evaluation of end-point sharpness for chelometric titrations based on pM *vs.* pH and pY *vs.* pH diagrams is proposed. The use of these diagrams to predict optimum titration conditions and conditions suitable for selective titrations is discussed. The pertinent equilibria controlling end-point sharpness are enumerated, and their effects on pM *vs.* pH and pY *vs.* pH curves are illustrated by reference to the titration of Mg, Ba, Pb and Zn with EDTA and various indicators. J. P. STERN

4664. **Investigations on spot-test papers.** G. Ackermann (Inst. f. anorg. Chem. der Bergakad. Freiberg/Sachsen, Germany). *Mikrochim. Acta*, 1959, (3), 357–369.—Studies on 69 varieties of filter-paper showed that the sensitivity of a reaction can be influenced by the exchange capacity as well as by the surface area of the drop. The sensitivity of the detection of cations is mainly determined by the exchange capacity, whereas the surface area of the drop is the primary determining factor in anion detection. D. F. PHILLIPS

4665. **Application of separating columns in analytical chemistry.** H. W. Kohlschütter, H. Getrost, G. Hofmann and H. H. Stamm (Eduard Zintl Inst. f. anorg. u. phys. Chem., Tech. Hochsch., Darmstadt). *Z. anal. Chem.*, 1959, **166** (4), 262–273.—Two substances in soln. may be separated by passage through a column if one of them undergoes some form of interaction with the column material. This has been applied to a study of the separation of $Cl^-$, $SO_4^{2-}$ and $PO_4^{3-}$ on a column of $Fe(OH)_3$, and to the separation of $Zn^{2+}$ and $Al^{3+}$ on a column of silica gel. T. R. ANDREW

4666. **New redox volumetric agents. VII. Titrations with vanadium(II) sulphate.** J. Vulterin (Dept. Chem. Ind., Sch. of Chem. Engng, Prague). *Chem. Listy*, 1959, **53** (4), 383–391.—A review of methods for the volumetric determination of organic and inorganic compounds by means of $VSO_4$ soln. is presented. (22 references.)

**VIII. Titrations with vanadyl sulphate and acetate.** J. Vulterin. *Ibid.*, 1959, **53** (4), 392–397.—A survey of titrations with vanadyl salts in acid and alkaline media is given. (25 references.)
J. ZÝKA

4667. **Use of potassium manganate in quantitative analysis. I. General.** G. den Boef (Anal. Chem. Lab., Univ. Amsterdam, Holland). *Z. anal. Chem.*, 1959, **166** (5), 321–325.—Oxidimetric titrations in alkaline soln. (0·5 to 4 *M*) can be carried out with manganate soln. Errors due to oxygen losses by the reduction of $KMnO_4$ to $MnO_2$ by some substances are minimised by this method.
B. B. BAUMINGER

4668. **Coulometric analysis.** V. A. Mirkin. *Zavod. Lab.*, 1959, **25** (3), 292–296.—A review is given, with 67 references. G. S. SMITH

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*See also Abstract*—**5042**, Analytical possibilities of micro-wave spectroscopy.

## 2.—INORGANIC ANALYSIS

*General, determination of elements (arranged in the order of the Periodic Table), analysis of minerals and inorganic industrial products.*

4669. **Separation and micro-identification of metal ions by solvent-extraction and ring-oven techniques.** P. W. West and Anil K. Mukherji (Louisiana State Univ., Baton Rouge, U.S.A.). *Anal. Chem.*, 1959, **31** (5), 947–950.—The combination of solvent-extraction and ring-oven techniques permits the separation and identification of 35 cations in one drop of aq. soln. The aq. cation chlorides in 7 *N* HCl are extracted with *iso*butyl methyl ketone - amyl acetate (2:1), when Sb, Au, Fe, V, Mo, Ga, As, Ge and Te appear in the ring formed by the organic phase. The aq. phase is then treated at pH 2 with 7 *M* $NH_4SCN$ (3 drops) and extracted with diethyl ether; the ether contains Co, Zn, Be and Sn. The aq. phase is then slowly extracted with acetylacetone, first at pH 2 (to extract Al, Cr, Cu, U, Zr and Ti) and then at pH 7 (to complete the extraction of Al). The aq. phase is then treated at pH 3 with 2% Na diethyldithiocarbamate soln. and immediately extracted with diethyl ether; Ni, Cd, Bi, Pb, Hg, Tl, W, Mn, Se and In pass into the ether. The final aq. residue contains Ba, Sr, Ca, Mg, Ce and Th. Spot tests for the identification of the individual cations in the rings are detailed.
J. P. STERN

4670. **Ion-exchange separations. Chromatographic separations based on ion charge.** J. S. Fritz and S. K. Karraker (Iowa State College, Ames, U.S.A.). *Anal. Chem.*, 1959, **31** (5), 921–923.—The greater affinity of a cation-exchange resin for a tervalent than for a bivalent cation permits the quant. separation of Zn from La. Thus 0·25 millimole of Zn is separated from 2·5 millimoles of La with a recovery > 99·4%. Bivalent ionic liquids (*e.g.*, ethylenediammonium chloride soln.) can be used in lower concn. as eluents than univalent liquids (*e.g.*, HCl). *Procedure*—Add the Zn or La soln. (approx. 0·01 *M* at pH < 3) (25 ml) at 15 ml per min. to the resin column (Dowex 50-X8 resin; diam. 12 or 21 mm) previously treated with 0·1 *M*

ethylenediammonium chloride. Elute with 0·1 *M* ethylenediammonium chloride (pH 3) and collect 10-ml fractions. Determine Zn and La by titration with 0·05 *M* EDTA, with "naphthylazoxine" [7-(1-naphthylazo)-8-hydroxyquinoline-5-sulphonic acid and arsenazo indicators, respectively.

J. P. STERN

4671. **Paper chromatography in the separation of ions. III. Separation of silver, copper and arsenic group elements.** A. K. Majumdar and M. M. Chakrabartty (Jadavpur Univ., Calcutta). *Anal. Chim. Acta*, 1958, **19** (2), 132–134.—The constants for the metal ions $Hg^{2+}$, $Ag^{+}$, $Pb^{2+}$, $Tl^{+}$, $Cu^{2+}$, $Cd^{2+}$, $Bi^{3+}$, $As^{3+}$ and $Sb^{3+}$ are determined by the technique and with the solvents previously used (*Anal. Abstr.*, 1959, **6**, 2177). The separation of mixtures containing up to five components appears feasible but, with the exception of $NH_4I$, the complexing agents give little advantage H. N. S.

4672. **Determination of aluminium, titanium and nickel in their alloys.** L. E. Hibbs and D. H. Wilkins (Res. Lab., General Electric Co., Schenectady, N.Y., U.S.A.). *Talanta*, 1959, **2** (1), 16–20.—The alloy is dissolved in aqua regia and, after destroying $HNO_3$, the soln. is passed through a column of Dowex-1 anion-exchange resin; Al, Ni and Ti are then eluted with 7 *M* HCl, leaving Co, Cu and Fe on the resin. The eluate containing Al, Ni and Ti is then passed through two columns connected in series containing, respectively, a cationic resin and an anionic resin. On eluting with 0·8 *M* HF - 0·06 *M* HCl the Al passes through both columns, the Ni is retained on the cationic resin and the Ti on the anionic resin. The columns are disconnected and Ni is eluted with 4 *M* HCl and Ti with 3 *M* HCl. The metal content of each of the three fractions is determined by titrating with EDTA and standard Cu soln. at pH 4·8, with calcein as fluorescent indicator (*cf.* Wilkins, *Anal. Abstr.*, 1959, **6**, 4419). W. T. CARTER

4673. **Amperometric titration method for the analysis of mixtures of bismuth, aluminium, calcium and magnesium salts.** Yuen-Kai Oong and Hwei-Chen Lee (Dept. of Anal. Chem., Nanking Pharm. Coll.). *Acta Pharm. Sinica*, 1959, **7** (3), 99–103.—The amperometric titration with 0·1 *M* EDTA at controlled pH and potentials (*cf.* Reilley *et al.*, *Anal. Abstr.*, 1956, **3**, 2401) has been applied to mixtures of the salts of Bi, Al, Ca and Mg. For $Bi^{3+}$, the test soln. is adjusted to pH 1·5 to 2 with 3 *N* NaOH and solid chloroacetic acid. The titration with EDTA is carried out in 0·0025% gelatin soln. and in the absence of air, at the applied potential of − 0·25 V *vs.* the S.C.E. For combined $Al^{3+}$, $Ca^{2+}$ and $Mg^{2+}$, after titration of $Bi^{3+}$, the soln. is treated with an excess of EDTA, adjusted to pH 4 and heated almost to boiling. The soln. is cooled and adjusted to pH 8 with aq. $NH_3$. The excess of EDTA is then back-titrated with 0·05 *N* $Ca(NO_3)_2$ at the applied potential of + 0·05 V *vs.* the S.C.E. For combined $Ca^{2+}$ and $Mg^{2+}$, triethanolamine is added to the test soln. to mask Al and Bi, and the pH is adjusted to 10 with 6 *N* $HNO_3$ before titration with EDTA at the applied potential of + 0·02 V *vs.* the S.C.E. For $Ca^{2+}$, $Bi^{3+}$ are previously removed from the test soln. (at pH 4) as sulphide. The soln. is then adjusted to pH 8 with dilute KOH soln.; $Zn^{2+}$ are added to serve as indicator. The titration with EDTA is carried out in the absence of air at the applied potential of − 1·6 V *vs.* the S.C.E. S. H. YUEN

4674. **Determination of nickel, zinc and aluminium in bronze and brass after determining copper, lead, tin and antimony by controlled-potential electrolysis.** B. Alfonsi (Lab. Auto-Avio, FIAT, Turin, Italy). *Anal. Chim. Acta*, 1959, **20** (3), 277–282.—Procedures are given for the successive determination of Ni, Zn and Al in the acid soln. remaining after the electrolytic separation of Cu, Pb, Sn and Sb (*Ibid.*, 1958, **19**, 276, 389, 569). The Ni is pptd. with dimethylglyoxime in slightly ammoniacal soln. at 45° to 50°, and the Zn in the filtrate is separated by controlled-potential electrolysis (0·4 to 0·8 amp., − 1·2 to − 1·55 V *vs.* the S.C.E.) in the presence of hydrazine hydrochloride. The Al is then determined in the final soln. by the addition of 8-hydroxyquinoline, dissolution of the oxinate in conc. $H_2SO_4$ and, after addition of $HClO_4$ and removal of any $SiO_2$, re-pptn. with ammonium benzoate at pH 3·6 to 4·2 in the presence of thioglycollic acid. Zinc should not be determined electrolytically if > 10 mg of Fe is present; if there is < 10 mg of Fe the amount co-deposited with the Zn should be determined. The accuracy is adequate for routine analysis. W. J. BAKER

4675. **Analysis of fission-product mixtures.** E. L. Geiger (Reynolds Electrical and Engng Co., Las Vegas, Nev., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 806–809.—A procedure is described for the rapid, sequential separation of radioactive Ru, Sr, rare-earth metals, Zr - Nb and Cs in air-filter, soil, sediment, vegetable and aqueous samples. The fission products are leached from the samples with a 3 *N* HCl - 0·1 *N* HF soln. and recoveries of 97% and individual decontamination factors > $10^3$ are obtained. A complete analysis requires 16 hr., and the precision of each analysis is within ± 4% at the 90% confidence limit. K. A. PROCTOR

4676. **Photometric determination of traces of hydrogen peroxide and copper(II) ions with phlorrhizin [phloridzin].** L. Erdey and J. Inczédy (Tech. Univ., Budapest). *Mikrochim. Acta*, 1959, (3), 438–444 (in German).—The increased oxidation potential of $H_2O_2$ in the presence of certain metal ions forms the basis of a sensitive colour reaction of phlorrhizin in the presence of $Cu^{2+}$, which is suitable for the photometric determination of $H_2O_2$ at pH 12. Similarly, traces of $Cu^{2+}$ can be determined at pH 9.

D. F. PHILLIPS

4677. **Relation between radiation intensity and concentration of the alkali metals in flame photometry.** N. S. Poluéktov and M. P. Nikonova (Inst. of Gen. and Inorg. Chem., Acad. Sci., UkrSSR). *Zavod. Lab.*, 1959, **25** (3), 263–268.—Apparent discrepancies between the experimental and theoretical shapes of the log intensity *vs.* log concn. curves are explained theoretically. G. S. SMITH

4678. **Influence of certain elements on the determination of the alkali metals by flame photometry.** T. K. Aldarov, A. E. Zak and E. S. Safonova. *Zavod. Lab.*, 1959, **25** (3), 269–271.—The effects of Na, K and Ni on the determination of Li, and the effects of Cd and Ni on the determination of K are studied, with particular reference to the analysis of electroplating soln. G. S. SMITH

4679. **Flame-photometric determination of oxides of alkali metals in tungstic acid.** R. Hamerník (Res. Lab., Tesla, Rožnov, Czechoslovakia). *Hutn. Listy*, 1959, **14** (2), 142–144.—Potassium and sodium can be separated from tungstic acid by heating the

sample with water acidified with HCl. The presence of sodium increases the colour intensity of the potassium flame, but a similar effect of potassium on sodium was not observed. Small amounts of Ca do not interfere. *Procedure*—Transfer the sample ($\simeq$ 2 g) to a 250-ml flask of resistance glass or silica, and add $H_2O$ (30 ml) and conc. HCl (5 to 7 drops). Heat under reflux for 2 hr. Separate the tungstic acid by filtering, wash with a small vol. of slightly acidified $H_2O$ (5 drops of conc. HCl in 100 ml of $H_2O$), dilute the filtrate to 100 ml and measure with a flame photometer. The error is $\gtrsim$ 0·002% of $K_2O$ or $Na_2O$. J. ZÝKA

4680. **Determination of lithium and potassium chlorides in the presence of each other by electrical conductivity.** J. Zatloukal (Res. Inst. Inorg. Chem., Ústí nad Labem, Czechoslovakia). *Chem. Průmysl*, 1959, **9** (3), 131–132.—The total amount of both elements is determined by evaporation. The residue is dissolved in a known vol. of $H_2O$, and the electrical conductivity is determined and compared with a calibration curve of standards containing various ratios of LiCl and KCl at constant total concn. For a ratio of LiCl to KCl of 1:1 an accuracy within $\pm$0·2% has been achieved, which changes to $\pm$1% if LiCl to KCl is 1:10, and to $\pm$10% if LiCl to KCl is 1:100. A Wheatstone bridge supplied with a.c. at 4 V and 50 c/s is used for the measurement and a Tesla Service oscillograph (with a transformer for increasing the sensitivity) for the indication of the balance point. J. ZÝKA

4681. **Flame-photometric determination of small amounts of sodium in silumins.** J. Weiss and B. Bieber (Res. Inst. of Materials and Technol., Brno, Czechoslovakia). *Hutn. Listy*, 1959, **14** (3), 247–248.—*Procedure*—Dissolve the finely ground sample (0·5 to 2·0 g) by boiling in a small porcelain beaker in HCl (1:1) (20 ml), cool, transfer to a 100-ml flask, dilute to vol. with twice-distilled $H_2O$, set aside and in an aliquot of the supernatant liquid (graphitic Si remains in the ppt.) determine the Na content with a Zeiss Model III flame photometer (filter Na 59, shade 40). Refer the results to a calibration curve. The procedure can be carried out in $<$ 20 to 30 min. with an accuracy of 0·002% of Na in samples containing 0·01 to 0·001% of Na. The results are not influenced by the presence of Mn (0·70%), Fe (1·50%), Ti (0·15%), Cu (1·80%), Zn (1%) or Mg (0·50%). For the determination of Na in the presence of Al, calibration curves for 0·5, 1·0 and 2·0 g of the sample with added $AlCl_3$ must be prepared. A suitable method is proposed for the preparation of Na-free $AlCl_3$ by crystallisation and pptn. in a current of HCl. J. ZÝKA

4682. **Adaptation of Winkler's method to the routine determination of alkali carbonate and hydroxide.** Z. Hošťálek (Dept. Inorg. Technol., Sch. of Chem. Technol., Prague). *Chem. Průmysl*, 1959, **9** (3), 123–125.—The sources of error in Winkler's method (the influence of phenolphthalein, pptn. of $BaCO_3$, addition of $BaCl_2$, influence of $CO_2$, decomposition of $BaCl_2$ with acid, concn. of acid and vol. of the soln.) have been systematically studied. The errors are influenced mainly by the ratio of the components to be determined. Conditions have been found for obtaining reproducible results and an empirical correction graph is given which eliminates systematic errors for the range of 0 to 95% of $CO_3^{2-}$ in the total anions. For samples containing $>$ 95% of $CO_3^{2-}$, Warder's method is preferred. *Procedure*—Dilute 25 ml of the sample soln. to 75 ml with $H_2O$, add $N$ $BaCl_2$ (35 ml) neutralised with $Ba(OH)_2$ or HCl to phenolphthalein, then phenolphthalein soln. (1% in 96% ethanol) (0·3 ml), mix thoroughly and titrate immediately with 0·5 $N$ to $N$ acid added dropwise. The time occupied must not exceed 3 min. Add methyl orange soln. (0·1%) (2 to 3 drops) and titrate with stirring till the soln. is red (pH about 3·9). Refer the results to a graph of observed values for the expression $(CO_3^{2-}/CO_3^{2-} + OH^-) \times 100$ *vs.* the true values. J. ZÝKA

4683. **Solubility of potassium tetraphenylboron in acetone - water solutions.** A. D. Scott, H. H. Hunziker and M. G. Reed (Agronomy Dept., Iowa State Coll., Ames, U.S.A.). *Chemist Analyst*, 1959, **48** (1), 11–12.—Results for the solubility of K tetraphenylboron (**I**) at 28° for acetone - water mixtures from 16 to 100% (v/v) of acetone are tabulated and presented as a graph. The solubility rises sharply from 1·2 mg per ml in a 32% soln. to 59·8 mg per ml in a 95% soln., and falls rapidly thereafter to 41·8 mg in 100% acetone. In analytical procedures in which pptd. **I** is dissolved in acetone and titrated with aq. soln., the acetone - water ratio should be kept as high as the conditions allow. R. E. ESSERY

4684. **Photometric determination of copper with diaminocyclohexanetetra-acetic acid [Complexone IV].** W. Nielsch (Karl-Reiss-Platz 12, Mannheim, Germany). *Mikrochim. Acta*, 1959, (3), 419–423.—In the pH range 5 to 11, Complexone IV forms with $Cu^{2+}$ a complex that has a max. extinction at 720 m$\mu$, which is independent of the type of buffer used and also of the acid used for dissolving the metal (*e.g.*, sheet copper). A favourable slope of the calibration curve is obtained. The method is suitable for the determination of Cu in the concn. range 20 to 110 $\mu$g per ml. No precision is quoted. D. F. PHILLIPS

4685. **Trace determination of copper and cobalt by chelate chromatography and dithizone photometry.** D. M. Smith and J. R. Hayes (Pennsylvania State Univ., University Park, U.S.A.). *Anal. Chem.*, 1959, **31** (5), 898–902.—Copper and Co ($\simeq$ 10 $\mu$g) are separated from each other and from $Fe^{3+}$ (10 mg), Mn (5 mg), Zn (10 mg), Cd (0·1 mg) and Ni (50 $\mu$g) by chromatography of the diethyldithiocarbamates on silica gel, with $CHCl_3$ - $CCl_4$ (1:1) (**I**) as developer. The elements are determined photometrically as dithizones in the eluate. *Procedure*—To the aq. metal nitrates add aq. $NH_3$ - $NH_4Cl$ buffer (pH 9·6 to 9·8) (25 ml), 10% $Na_4P_2O_7$ soln. (15 ml) and 0·1% Na diethyldithiocarbamate soln. (2 ml), and after 1 min. extract with $CCl_4$ (3 $\times$ 3 ml). Pass the extract through 3 g of silicic acid activated at 500° for 24 hr.; the flow rate should be 0·5 ml per min. through a column 7·5 cm deep. Elute the Cu and Co with **I** for 1 to 2 hr. (flow rate 0·3 to 0·4 ml per min.). Destroy the complexes with conc. $H_2SO_4$ (0·75 ml) and 60% $HClO_4$ (0·3 ml) at 200° to 250°. Dilute and neutralise the soln. and convert the Cu and Co into the dithizones for photometry at 510 and 545 m$\mu$, respectively. J. P. STERN

4686. **Concentration of traces of silver contained in lead by a precipitation method.** Z. Zagórski and O. Kempiński (Anal. Lab., Central Lab. of Accumulators and Cells, Poznan, Poland). *Chem.*

*Anal., Warsaw*, 1959, **4** (1–2), 422–432.—Errors due to the adsorption of AgCl on the $PbSO_4$ ppt. are minimised by the use of *p*-dimethylaminobenzylidenerhodanine for the concentration of Ag by pptn. This method, in conjunction with a polarographic determination of the Ag, provides a useful means of determining the amount of Ag ($< 0{\cdot}0005\%$) in all commercial grades of lead, and in alloys containing Sb and in metallic cadmium. Errors are $> 4\%$ and the sensitivity of the method may be increased about 50 times by increasing the sample and diminishing the volume of polarographic soln. to the micro-analytical scale. The method is useful in controlling the purification of lead salts, and in the preparation of spectral standards. W. B. MIASKOWSKI

4687. **Determination of copper, iron and lead in metallic silver.** W. Kemula, K. Brajter, S. Cieślik and H. Lipińska (Dept. of Inorg. Chem., Univ., Warsaw). *Chem. Anal., Warsaw*, 1959, **4** (1–2), 409–415.—By the method described, 0·02 to 0·05 % of Cu, 0·006 to 0·01% of Fe and $\simeq 0{\cdot}003\%$ of Pb can be determined. The sample is dissolved in conc. $HNO_3$, evaporated and diluted with $H_2O$. This soln. is passed through a cation-exchange column (Wofatit KPS-200), which is then treated successively with *N* KCl to precipitate AgCl, with ammonium salicylate to elute $Fe^{3+}$ and with HCl to elute $Pb^{2+}$ and $Cu^{2+}$. The latter eluate is added to an anion-exchange column (Wofatit 150-L); Pb is retained and can be eluted with 0·001 *N* $HNO_3$. The separated cations are determined polarographically—$Fe^{III}$ in *N* aq. $NH_3$ and ammonium salicylate as supporting electrolyte, Cu in 1·5 *N* aq. $NH_3$ with 1·5 *N* $NH_4Cl$, and Pb in *N* $KNO_3$. W. B. MIASKOWSKI

4688. **Detection of beryllium with acetylacetone.** R. D. Cool (Madison Coll., Harrisonburg, Va., U.S.A.). *Chemist Analyst*, 1959, **48** (1), 7–8.—Place a drop of test soln. on a slide and invert it over conc. aq. $NH_3$. Remove the liquid from the pptd. $Be(OH)_2$ with a capillary, and treat the washed residue with just enough satd. aq. acetylacetone soln. to dissolve the ppt. When oily drops appear, or crystallisation starts at the edge of the drop, draw a fine-tipped glass rod through the oily or crystallised area and across the drop. In the presence of Be, characteristic right-angled crystals appear, which are examined under a magnification of × 50, along the track of the rod. The limit of certain detection is 0·1 μg. When 0·5- and 1-μg amounts of Be were used with 10 times these amounts of other metals, interference was observed with Al, Bi, $As^V$, Ce, Cr, Ga, In, Fe, La, Mn, Nd, Pr, Ru, Sm, Sc, Tm, $Sn^{II}$, $Sn^{IV}$ and Zr. No interference was observed with $As^{III}$ and 43 other metals. R. E. ESSERY

4689. **Quantitative spectrographic analysis of magnesium alloys.** J. Fijalkowski (Lab. of Aviation Materials, Aviation Inst., Warsaw). *Chem. Anal., Warsaw*, 1959, **4** (1–2), 455–461.—A modified method is described permitting the simultaneous determination of alloy components, *e.g.*, Al, Zn and Mn, and impurities, *e.g.*, Fe, Cu, Si and Ni. Details are given of the equipment used, the conditions of analysis, and the results obtained by testing various line-pairs. The coeff. of variation for individual elements ranges from ±4 to 7%, except for Si, when it reaches 9%. W. B. MIASKOWSKI

4690. **Electrochromatography in the separation of ions. VII. Separation of alkaline-earth metals.** A. K. Majumdar and B. R. Singh (Jadavpur Univ., Calcutta, India). *Anal. Chim. Acta*, 1959, **20** (3), 275–277.—By using the procedure described previously (Majumdar and Mukherjee, *Anal. Chim. Acta*, 1956, **15**, 547), complete separation of ternary mixtures of $Ca^{2+}$, $Mg^{2+}$ and $Sr^{2+}$ or $Ba^{2+}$ can be made with 0·1 *N* $NH_4Cl$ as electrolyte, and less complete but detectable separation with 0·1 *N* $NH_4NO_3$. Binary separations (Ca - Ba, Ca - Sr, Ca - Mg, Mg - Sr and Mg - Ba) can be achieved with other electrolytes, *e.g.*, $HNO_3$, NaCl, acetic acid, aq. thiourea and Na rhodizonate. Movements (in cm) of the ions are listed. W. J. BAKER

4691. **Visual EGTA [1:2-di-(2-aminoethoxy)-ethane-NNN'N'-tetra-acetic acid] titration of calcium in the presence of magnesium.** F. S. Sadek, R. W. Schmid and C. N. Reilley (Dept. of Chem., Univ. of N. Carolina, Chapel Hill, U.S.A.). *Talanta*, 1959, **2** (1), 38–51.—Calcium can be selectively titrated in the presence of Mg with EGTA, with zincon (2-carboxy-2'-hydroxy-5'-sulphoformazylbenzene) as indicator. The Mg can then be titrated in the same soln. with EDTA (disodium salt). *Procedure*—Neutralise the sample soln. and adjust to pH 9·5 with aq. $NH_3$ - $NH_4NO_3$ buffer. Add zincon soln. (0·2%) (2 to 3 drops) and sufficient of a soln. of EGTA (containing the stoicheiometric amount of Zn) to give a permanent blue colour. Titrate the Ca with a standard soln. of EGTA. Add KCN soln. and titrate the Mg with standard EDTA (disodium salt) soln., with Eriochrome black T as indicator. When Zn is present it can be determined by titration with standard tetraethylenepentamine dihydrosulphate soln. and zincon before the titration of Ca. The procedure can be used for the analysis of soln. containing Ca and Mg in ratios of up to 1:20, with an accuracy of ± 0·2% at the 5-mg level. A theoretical treatment is given of the equilibria involved in the titrations. W. T. CARTER

4692. **New sensitive spot reaction for zinc.** V. Anger (Lab. Dr. V. Anger, Vienna 18). *Mikrochim. Acta*, 1959, (3), 473–475.—The detection of 0·05 μg of Zn in neutral or acid soln. at a limiting concn. of 1 p.p.m. is possible with trisodium pentacyano-NN-dimethyl-*p*-nitrosoanilinoferrate. In the presence of Zn a green ring appears which, on spotting with 2 *N* $H_2SO_4$, changes to blue, while the pale-green colour of the reagent is completely discharged. Mercury, Cu, Cd, Co, Ni, Fe and $UO_2^{2+}$ interfere through formation of dark-green rings; $Fe^{3+}$ may be masked by fluoride. Zinc may be detected in the presence of Cu, Cd and Ni after treatment of the ammoniacal test-soln. with colourless ammonium sulphide and subsequent separation of the ZnS with 2 *N* $H_2SO_4$ or HCl. This enables 2 μg of Zn to be detected in the presence of 1500-fold amounts of Cu, Cd and Ni. The reagent may also be used to detect 0·5 μg of Cd in the presence of 100-fold amounts of Cu. D. F. PHILLIPS

4693. **Use of EDTA to eliminate interference in the zinc - ferrocyanide titration.** D. G. Davis and H. T. McLendon (Sch. of Chem., Georgia Inst. of Technol., Atlanta, U.S.A.). *Talanta*, 1959, **2** (2), 124–127.—The use of EDTA as a complexing agent for interfering metal ions is studied. For the detection of the end-point, the relative merits of potentiometric methods and of amperometric methods, using a manual polarograph and either one or two indicator electrodes, are discussed.

Amperometric methods are easier and more accurate. If the pH is controlled at 2·0 to 2·1, EDTA, sufficient to complex all the interfering metals, with an excess equivalent to approx. one-half of the Zn, eliminates interference due to Ni, Fe and Pb, while Al, Mn, $Cl^-$ and $SO_4^{2-}$ do not interfere either in the presence or absence of EDTA. Interference by Cu cannot be removed by EDTA. Thiosulphate is not satisfactory for masking Cu, while hydrazine sulphate is only useful when the Cu is much smaller in amount than the Zn. For most alloys, it is best to remove Cu by electrolysis, and then eliminate the remaining interferences with EDTA. R. E. ESSERY

4694. **Use of complexometric titration in the control of galvanising baths.** I. Dubský (Jablonecká Bižuterie n.p., Jablonec n. Nis., Czechoslovakia). *Chem. Průmysl*, 1959, **9** (2), 80–84.—Cyanide complexes of Zn and Cd react with acetone, ethyl methyl ketone, *cyclo*hexanone or benzaldehyde, and the liberated $Zn^{2+}$ or $Cd^{2+}$ can be titrated with EDTA (disodium salt) (**I**). The complexes of Cu, Ni, Co, Fe and Hg do not react in a similar way. *Procedure for Zn*—Dilute the sample to 10 to 30 ml, add pure acetone (30 to 50 ml), buffer soln. (pH 10) ($NH_4Cl$ - aq. $NH_3$), and Eriochrome black T as indicator and titrate with **I** till blue. When titrating Cd an excess of **I** is added and the excess back-titrated with $MgSO_4$ soln. J. ZÝKA

4695. **Detection of cadmium by selective paper chromatography.** M. Ziegler and H. Winkler (Anorg.-chem. Inst., Univ., Göttingen). *Z. anal. Chem.*, 1959, **166** (4), 241–242.—Cadmium (5 μg) may be detected in the presence of $Cu^{2+}$, $Pb^{2+}$, $Bi^{3+}$ (all in 2000-fold excess) or $Hg^{2+}$ (100-fold excess) by transferring a drop of soln. to a paper strip and developing it for 1 hr. with a solvent prepared by shaking 3 vol. of *n*-butanol with 1 vol. of HCl (3 *N*) and saturating the organic phase with $H_2S$. Only $Cd^{2+}$ migrate under these conditions, and the spot is detected by spraying the paper with $(NH_4)_2S$ soln. T. R. ANDREW

4696. **High-frequency titrations. II. The mercury(II) - thiocyanate reaction.** Anil K. Mukherji and Bharat R. Sant (Louisiana State Univ., Baton Rouge, U.S.A.). *Anal. Chim. Acta*, 1959, **20** (3), 259–262.—With the apparatus and procedure described previously (Sant and Mukherji, *Ibid.*, 1959, **20**, 124), the oscillometric titration of $Hg(NO_3)_2$ soln. with aq. KSCN soln. gives one inflection corresponding to the quant. formation of $Hg(SCN)_2$, whilst in the reverse titration $Hg(SCN)^+$ are formed. This method can be used for the rapid micro-determination of either $Hg^{2+}$ or $SCN^-$ in very dil. soln. The accuracy is high; only in the range of 0·00003 to 0·00006 *M* does the error become 2 to 4%. The titration can be made in the presence of $HNO_3$ provided that the total acidity in the system is $\geq$ 0·003 *N*. W. J. BAKER

4697. **Direct thermometric titration of boric acid.** F. J. Miller and P. F. Thomason (Anal. Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Talanta*, 1959, **2** (2), 109–114.—Apparatus and procedure are described for the automatic thermometric titration of $H_3BO_3$, a thermistor and bridge with automatic recording being used (*cf.* Linde *et al.*, *Brit. Abstr. C*, 1953, 330). The chart records the increase of potential as the titration proceeds, and the distance travelled by the chart is calibrated in terms of the vol. of titrant added from the burette. The beginning and end of the titration are marked by turning-points on the curve. Although not essential for a good titration, the addition of mannitol improves the shape of the curve. In the presence of strong acid, both this and the $H_3BO_3$ can be titrated sequentially. Amounts of $H_3BO_3$ in the region of 0·3 milli-equiv. can be determined with a coeff. of variation of 1%. R. E. ESSERY

4698. **Determination of boric acid in methyl borate.** I. I. Strizhevskiĭ (All-Union Sci. Res. Inst. of Autogenous Treatment of Metals). *Zavod. Lab.*, 1959, **25** (2), 146.—Free boric acid is determined from the amount of water (3 moles for 1 mole of boric acid) obtained by reaction with methanol in the presence of pyridinium iodide soln. G. S. SMITH

4699. **Separation of aluminium and iron from copper, nickel, zinc and manganese on cationites. Application to the analysis of copper alloys.** Z. Marczenko (Anal. Dept., Inst. of Gen. Chem., Warsaw). *Chem. Anal., Warsaw*, 1959, **4** (1–2), 437–444.—By the use of a column of cationite (Wofatit P, Dowex 50 or SBS, ammonium form) it is possible to separate, with a high degree of accuracy, Al and Fe from Cu, Ni and Zn, using sulphosalicylic acid as complexing agent. Good results in the separation of Al plus Fe from Cu plus Ni plus Zn were obtained on all three cationites in strongly ammoniacal medium, and on Wofatit P and Dowex 50 also in weakly ammoniacal medium (pH $\simeq$ 9). In each case an attempt to separate Al plus Fe from Mn proved unsuccessful. W. B. MIASKOWSKI

4700. **Study of the chemistry of scandium on a tracer scale with scandium-46.** B. C. Purkayastha and V. R. Pai Verneker (Inst. of Nuclear Physics, Calcutta, India). *Anal. Chem.*, 1959, **31** (5), 814–815.—A study of the mixed crystal formation of ferric sulphate containing tracer amounts of Sc, Y and Eu indicates that Sc has a greater resemblance to the iron family than to the rare-earth elements. K. A. PROCTOR

4701. **Spectrophotometric determination of cerium in fluoride salts.** J. C. White and R. F. Apple (Anal. Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Talanta*, 1959, **2** (2), 176–182.—Tervalent Ce in fluoride salt mixtures is determined by measurement of its u.v. peak at 253 mμ in 3 *M* HCl. Weigh the sample (2 to 5 g) into a platinum dish, add 1 g of $H_3BO_3$ and mix. Add conc. $HNO_3$ (5 ml), conc. HCl (20 ml) and conc. $H_2SO_4$ (25 ml) and heat to strong fumes. Cool, and dilute to 500 ml with water. Transfer an aliquot ($\geq$ 10 ml, containing 0·5 to 5 mg of Ce) to a centrifuge tube. Add conc. aq. $NH_3$ dropwise till the Ce is pptd., and 2 ml in excess. Centrifuge for 2 min., decant the supernatant liquid and dissolve the ppt. in 10 ml of 7 *M* HCl, making up to 25 ml with the same acid. Transfer to a separating-funnel, add 5 ml of 0·05 *M* tri-*n*-octylphosphine oxide in *cyclo*hexane, shake for 2 min., and allow to separate. Measure the extinction of the aq. phase against water at 253 mμ. Beer's law is obeyed up to 0·4 mg of Ce per ml. Interfering elements are removed either by the pptn. or the extraction, but $Cr^{VI}$ is reduced to $Cr^{III}$ in 7 *M* HCl, and this is not extracted. Chromium in amount three times that of the Ce introduces a 4% error, but it is rarely present in fluoride salts in amounts large enough to cause

difficulty. Over a range from 0·4 to 8·9% of Ce, the average difference between results by the present method and radio-tracer methods was < 2%. R. E. ESSERY

4702. **X-ray emission spectrographic analysis of high-purity rare-earth oxides.** F. W. Lytle and H. H. Heady (Rare and Precious Metals Expt. Station, U.S. Bureau of Mines, Reno, Nev.). *Anal. Chem.*, 1959, **31** (5), 809–811.—Small amounts (0·01 to 1·0%) of rare-earth elements can be determined by this method with an average error of ≃ 10%. The method is dependent on the accurate determination of the spectral line intensity above the background. The preparation of the sample and standards, the choice of analytical lines and the use of a helium atmosphere for the optical path to increase the intensities are discussed. K. A. PROCTOR

4703. **Emission spectrographic double-arc analysis of readily volatile trace elements in graphite.** I. Janda and E. Schroll (Mineralog. Inst., Univ., Vienna). *Mikrochim. Acta*, 1959, (3), 389–401.—The procedure of Ahrens ("Quantitative Spectrochemical Analysis of Silicates," 1954, London) for double-arc analysis has been modified and applied to the determination of As, Ag, Sb, Cd, Cu, Ga, Ge, Hg, Mo, Pb, Sn, Tl and Zn present as traces in graphitic and carbonaceous rocks. A special holder was devised for the Ahrens-type micro graphite crucible and the work was carried out in a Zeiss Qu 24 medium quartz spectrograph, with a three-step filter (100, 20 and 4% transmission). The samples were prepared by mixing the finely ground substance with $Li_2CO_3$ and $(NH_4)_2SO_4$ in the proportions of 15:3:1, respectively, to give a total crucible charge of 0·4 g. Excitation was by d.c. arc at 110 V and 7 to 10 amp. Detection limits of from 0·03 to 30 p.p.m. were attained. By using photometric evaluation with background correction, reproducibilities of ± 2 to ± 16% were obtained for individual exposures. D. F. PHILLIPS

4704. **Rapid method for determination of small amounts of carbon monoxide in gas mixtures.** I. Lysyj, J. E. Zarembo and A. Hanley (Food Machinery and Chemical Corp., Princeton, N.J., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 902–904.—Direct weighing of the $CO_2$, produced by the oxidation of CO over a decomposed $AgMnO_4$ catalyst, and absorbed on Ascarite, permits 0·3 to 1·5% of CO to be determined with an accuracy within ± 0·85% in a gas sample (500 ml) containing N (75 to 78%), O (18 to 21%) and unsaturated hydrocarbons (1 to 5%). The absorption train comprises Mersil (164 g of red HgO dissolved in 715 ml of cold 29% $H_2SO_4$; in this soln. is dissolved 480 g of $MgSO_4.7H_2O$, the product is filtered and mixed with enough silica gel to give a moist mass, which is dried at 100°) and anhydrone - Ascarite absorption bulbs, a combustion tube containing $AgMnO_4$ at 450° to 500°, an anhydrone absorption tube, the weighed Ascarite absorption tube, and a guard tube. The train is purged with O (20 to 40 ml per min. for 10 to 15 min.) and the sample then passed at 20 to 30 ml per min.; finally the train is purged again with O for a further 15 min. J. P. STERN

4705. **Rapid determination of carbonates.** F. L. Hahn (Angel Urraza 718-303, Mexico 12, D.F., Mexico). *Z. anal. Chem.*, 1959, **166** (4), 243–246.—The $CO_3^{2-}$ content of washing powders, etc., has been determined by evolution of $CO_2$ with acid and subsequent absorption in NaOH so ln. in a simple apparatus. T. R. ANDREW

4706. **Determination of silicic acid by distillation of fluorosilicic acid in a silver apparatus.** P. Ehrlich and T. Keil (Anorg. Abt. des Chem. Inst. der Univ. Giessen). *Z. anal. Chem.*, 1959, **166** (4), 254–261.—From 10 to 150 μg of $SiO_2$ may be determined in the presence of 1 g of $TiO_2$, $V_2O_5$, $ZrO_2$ or $Al_2O_3$ by the steam-distillation of $H_2SiF_6$ from a soln. containing $H_2SO_4$ and HF in a silver apparatus, and subsequent photometric determination as molybdenum blue. The distillate is neutralised to *p*-nitrophenol and to an aliquot is added 15 ml of $H_3BO_3$ - $(NH_4)_6Mo_7O_{24}$ soln. [25 g of $H_3BO_3$ 30 ml of HCl (sp. gr. 1·16) and in 400 ml of $H_2O$ mixed with 10 g of $(NH_4)_6Mo_7O_{24}.4H_2O$ in 250 ml of $H_2O$ and diluted to 1 litre] and the mixture is set aside for 5 min.; 10% citric acid soln. (4 ml) is added and the soln. diluted to 49 ml; $SnCl_2$ soln. [1·2% in HCl (1:5)] (1 ml) is added and the extinction is measured at 660 mμ. A precision of ± 2% is claimed in the range 50 to 150 μg of $SiO_2$. T. R. ANDREW

4707. **Analysis of used silicon - copper alloys [employed in the synthesis of chlorosilanes].** A. P. Terent'ev, B. M. Luskina and S. V. Syavtsillo. *Zavod. Lab.*, 1959, **25** (3), 288–289.—Determinations of C, Cl, Si, Cu and Fe on a single sample are described. Wet combustion of the sample (0·2 to 1·5 g) is carried out in a flask containing 10 ml of conc. $H_2SO_4$ and 3 to 4 ml of $CrO_3$ soln. (70 g of $CrO_3$ dissolved in 100 ml of water) in a current of O. The oxidation products pass through a heated (700° to 750°) quartz tube containing pumice which has been soaked in 10% $(NH_4)_2Cr_2O_7$ soln. and ignited. The absorption of Cl and HCl takes place in a vessel containing hydrazine hydrate and acetic acid at pH 6 (a soln. that does not absorb $CO_2$), and $CO_2$ is absorbed in soda asbestos. The contents of the reaction flask are heated with a few drops of methanol or ethanol together with 40 to 50 ml of water, and the insoluble matter (free Si with small amounts of $SiO_2$, SiC, etc.) is filtered off, washed, and dried to const. wt. at 110° to 130°. In the filtrate Cu and Fe are determined by known methods. G. S. SMITH

4708. **Use of naphthalene derivatives in inorganic analysis. VII. The nitronaphthols as fluorimetric reagents for stannous tin.** J. R. A. Anderson, A. J. Costoulas and J. L. Garnett (N.S.W. Univ. of Technol., Sydney, Australia). *Anal. Chim. Acta*, 1959, **20** (3), 236–242.—Thirteen nitro derivatives of 1-naphthol and 2-naphthol are listed that can be used for the fluorimetric detection of $Sn^{II}$ in concn. as low as $10^{-4}$ to $10^{-5}$ g. The 2-nitro compounds give a more intense fluorescence than do the 1-nitro compounds; 8-nitro-1-naphthol is least reactive. *Procedure*—Place a drop of the sample soln. on Whatman No. 1 chromatographic paper and spray the air-dried spot with a 0·1% soln. of the reagent in a mixture (1:1, by vol.) of 96% ethanol and 10 *N* HCl. Then spray the dry paper with 15 *N* aq. $NH_3$, again air-dry and view under u.v. light. The fluorescence is specific for $Sn^{2+}$. W. J. BAKER

4709. **Determination of lead by the anodic amperometric method.** V. A. Khadeev and A. G. Nikurashina (V. I. Lenin Central Asia State Univ.). *Zavod. Lab.*, 1959, **25** (3), 283–285.—The method is

based on the current due to the oxidation of $Pb^{2+}$ to $PbO_2$ at a rotating platinum electrode, and titration is carried out with $K_2Cr_2O_7$ soln. at a potential of 1 V *vs.* the S.C.E. in the presence of an acetate buffer soln. of pH $\simeq$ 4. With contents of Pb < 0·2 mg per ml, the soln. should contain 10 to 15% of ethanol. No interference is caused by Mn and Ni at concn. $\geqslant$ twice the concn. of Pb. Even small amounts of Co interfere. The method is applied to the determination of Pb (4·33%) in leaded bronze. An aliquot (25 ml) of the soln. of the alloy is boiled and treated with 0·5 ml of 1·5 *M* acetate buffer soln., then cooled and titrated. G. S. SMITH

4710. **Determination of lead in plating electrolytes, using ethylenediaminetetra-acetic acid (disodium salt) and Xylenol orange indicator.** K. E. Langford. *Electroplating*, 1959, **12** (3), 103, 119.—From a study of the volumetric determination of Pb, the following method is recommended. Dilute 1 ml of test soln. to 400 ml with water, add 0·5 to 1 g of hydroxyammonium chloride, 6 to 8 drops of a 1% aq. soln. of Xylenol orange and 1 g of hexamine, and titrate with 0·2 *N* EDTA (disodium salt) to a pale-yellow end-point. The titration is accurate to within 0·05 ml.

C. H. COWPER-COLES

4711. **Spectrographic determination of small quantities of antimony and tin in lead after a preliminary concentration by co-precipitation.** J. Downarowicz and Z. Zagórski (Anal. Lab., Central Lab. of Accumulators and Cells, Poznan, Poland). *Chem. Anal., Warsaw*, 1959, **4** (1–2), 445–454.—Small amounts of Sb and Sn in lead can be determined spectrographically after co-pptn. with $MnO_2$ as collector; an almost 200-fold concentration is achieved, thus permitting the determination of 0·001% of Sb and 0·0005% of Sn. The method is designed for a quartz spectrograph of medium dispersion and the samples are excited by means of an a.c. arc between carbon electrodes. The manganese spectrum served as reference spectrum and the following line-pairs were used—for Sb and Sn from 0·01 to 0·1%, Sb 2878 A or Sn 2863 A and Mn 2915 A; for Sb from 0·001 to 0·01%, Sb 2311 A, Mn 2305 A; for Sn from 0·0005 to 0·01%, Sn 2355 A, Mn 2473 A. The relative error is $\geqslant$ 12% for Sb and 20% for Sn. W. B. MIASKOWSKI

4712. **Rapid volumetric method for determining titanium in ferrotitanium.** E. F. Konstantinov (Stalin Metallurgical Works). *Zavod. Lab.*, 1959, **25** (2), 134–136.—The alloy is dissolved in dil. $H_2SO_4$ in an atmosphere of $CO_2$ and the $Ti^{3+}$ are titrated with a soln. of $Fe^{3+}$. Since $Ti^{4+}$ are not formed no special reduction stage is required.

G. S. SMITH

4713. **Determination of small amounts of titanium in tin alloys.** O. I. Popova (Inst. of Metal Ceramics and Special Alloys, Acad. Sci., UkrSSR). *Zavod. Lab.*, 1959, **25** (2), 148.—The sample (0·5 to 1 g) is dissolved in 10 to 15 ml of conc. $H_2SO_4$ and the cooled soln. is treated with 0·5 ml of 1% chromotropic acid soln. and diluted to 25 ml with conc. $H_2SO_4$. The colour intensity is compared with that of a scale of standards. No interference is caused by Sn, Nb and Ta. The method is applicable to contents of Ti between 0·001 and 0·007%.

G. S. SMITH

4714. **Polarographic determination of quadrivalent titanium in the presence of foreign ions in orthophosphoric acid as electrolyte.** P. Szarvas, L. Máczay and A. Gergely (Inst. for Inorg. and Anal. Chem., L. Kossuth Sci. Univ., Debrecen, Hungary). *Magyar Kém. Foly.*, 1959, **65** (2), 69–72.—The polarographic determination of $Ti^{IV}$ in 2 *M* $H_3PO_4$ is described: $E_{\frac{1}{2}} = -0{\cdot}229$ V. The polarogram is not influenced by a 100-fold excess of $Cd^{II}$, $Co^{II}$ or $Ni^{II}$, or a 10-fold excess of $Mn^{II}$. If these ions are present together, a 20-fold excess of $Cd^{II}$, $Co^{II}$ and $Ni^{II}$, or a 10-fold excess of all these plus $Mn^{II}$ does not interfere; $Fe^{III}$, $V^{V}$, $Cr^{III}$ or $W^{VI}$ in an amount equal to that of $Ti^{IV}$ does not interfere, but very small amounts of $Mo^{VI}$ do.

A. G. PETO

4715. **Application of infra-red spectroscopy to the analysis of titanium tetrachloride.** D. I. Tsekhovol'skaya, T. A. Zavaritskaya, G. S. Denisov and V. M. Chulanovskiĭ (All-Union Aluminium-Magnesium Inst.). *Zavod. Lab.*, 1959, **25** (3), 300–302.—The determination of HCl (at 2830 or 2929 $cm^{-1}$), of $TiOCl_2$ (at 821), of $VOCl_3$ (at 2061), of $COCl_2$ (at 1654 or 1812), of hexachlorobenzene (at 1301), of dichloroacetyl chloride (at 1779 or 1809), of trichloroacetyl chloride (at 1802), of chloroacetyl chloride (at 1785 or 1820), and of $CO_2$ (at 2338) is described. The method can be used for determining the solubility of $CO_2$, HCl, $COCl_2$ and hexachlorobenzene in $TiCl_4$. In the presence of excess of $TiCl_4$, hydrolysis takes place in accordance with the equation—

$$TiCl_4 + H_2O = TiOCl_2 + 2\ HCl.$$

G. S. SMITH

4716. **Analytical applications of Xylenol orange. I. Determination of traces of zirconium.** K. L. Cheng (Metals Div., Kelsey-Hayes Co., Utica, N.Y., U.S.A.). *Talanta*, 1959, **2** (1), 61–66.—Zirconium (5 to 60 $\mu$g) can be determined by measuring the extinction of the complex formed with Xylenol orange in 0·2 *N* $H_2SO_4$. *Procedure*—To the neutral sample soln. add $H_2SO_4$ (2·5 *N*) (2 ml) or $HClO_4$ (5 *N*) (4 ml) and aq. Xylenol orange soln. (0·05%) (2 ml). Dilute to 25 ml and measure the extinction at 535 m$\mu$. Niobium, Hf, Mo, Bi, $Fe^{III}$ and $Sn^{II}$ interfere, but the effect of Nb, Mo and $Sn^{II}$ can be eliminated by carrying out the test in 0·3 to 0·5 *N* $H_2SO_4$; $Fe^{III}$ can be masked with ascorbic acid and Bi with $Cl^-$. Fluoride, EDTA, nitrilotriacetic acid, citrate, tartrate, oxalate, thiosulphate and phosphate also interfere.

W. T. CARTER

4717. **Volumetric determination of zirconium. II. The oxidation of zirconium tetramandelate with chromic acid.** A. Schneer and H. Hartmann (Inst. of Gen. and Inorg. Chem., L. Eötvös Sci. Univ., Budapest). *Magyar Kém. Foly.*, 1959, **65** (2), 64–69.—Mandelic acid selectively precipitates Zr in HCl soln. Collect the tetramandelate, dissolve it in conc. $H_2SO_4$ and add it to 0·25 *N* $Na_2Cr_2O_7$ in conc. $H_2SO_4$. Add sufficient water to make it 80 to 90% (w/w) with respect to $H_2SO_4$, and $\simeq$ 0·06 *N* with respect to $Na_2Cr_2O_7$; heat in an air bath at 115° for 20 min. and back-titrate the excess of $Na_2Cr_2O_7$ with $FeSO_4$ soln. with ferroin as indicator; 1 ml of 0·1 *N* $Na_2Cr_2O_7 \equiv 67{\cdot}07$ $\mu$g of Zr. When 0·5 to 5 mg of Zr is present, a + 2% correction will give an accuracy of $\pm$ 1% but, if only 0·1 to 0·5 mg of Zr is present, the error may be $\pm$ 10%. The method can be used for rocks containing 0·01 to 0·1% of Zr. Compounds forming a hydrated oxide in acid soln. do not interfere. The

chromatometric determination of mandelic acid is also described. A. G. PETO

4718. **Rapid complexometric determination of zirconium in zirconium glass and concentrates.** V. I. Panasyuk and N. A. Miroevskaya (All-Union Sci. Res. Inst. of Glass Fibre). *Zavod. Lab.*, 1959, **25** (2), 147.—A simplified modification of the method of Goryushina and Romanova (*cf. Anal. Abstr.*, 1958, **5**, 1484) is presented. With concentrates of Zr, technical dioxide or zirconium glass the sample (0·2 g) is fused in a silver crucible with a mixture of 5 g of KOH and 2 g of $Na_2B_4O_7$ and the aq. soln. of the melt, together with insoluble matter, is treated with 50 ml of conc. HCl and the whole diluted to 250 ml. An aliquot (25 ml) is boiled with 25 ml of 2 *N* HCl and 50 ml of water and titrated with 0·05 *N* EDTA (disodium salt) to Eriochrome black T, the final end-point being obtained after further heating. G. S. SMITH

4719. **Complexometric determination of zirconium in borides and nitrides.** E. I. Nikitina. *Zavod. Lab.*, 1959, **25** (2), 142.—With borides, 0·2 g is dissolved in 20 ml of dil. $H_2SO_4$ (1:1) and 5 ml of conc. $HNO_3$, oxides of N are boiled off, the insoluble matter (carbide) is separated and fused with $K_2S_2O_7$, and the aq. soln. of the melt is combined with the main soln., which is then diluted to 100 ml. With nitrides, 0·2 g is dissolved in 20 ml of conc. $H_2SO_4$, the soln. is evaporated to fuming, and the cooled soln. is diluted to 100 ml. For the titration, 50 ml is mixed with an accurately measured amount (10 to 25 ml) of 0·1 *N* EDTA (disodium salt), 20 ml of 20% tartaric acid soln., 2 ml of ammonium acetate soln. (concn. not stated) and 2 drops of Tropaeolin OO (C.I. Acid Orange 5) indicator soln., and treated with aq. $NH_3$ to give a pale pink colour. The soln. is boiled for 10 min. (to dissolve a pptd. complex of Zr and EDTA), then cooled and mixed with 1 g of thiourea, and titrated with a soln. of $Bi(NO_3)_3$ to the appearance of a bright yellow colour. G. S. SMITH

4720. **[Determination of] thorium in stone meteorites by neutron activation analysis.** G. L. Bate, J. R. Huizenga and H. A. Potratz (Argonne Nat. Lab., Lemont, Illinois). *Geochim. et Cosmoch. Acta*, 1959, **16** (1–3), 88–100.—Full details are given for the preparation and slow neutron activation of the samples, during which $^{232}Th$ by slow neutron absorption produces $^{233}Th$ which decays with a 23-min. half-life to $^{233}Pa$. Radiochemical assays are based on $^{233}Pa$ because of the latter's longer half-life and its intense $\gamma$-radiation of 310-keV energy which permits convenient detection by scintillation counting. The procedures for separation of Pa are based on its co-deposition with certain precipitates (especially manganese dioxide and barium fluorozirconate), extraction into appropriate organic solvents, and pronounced complexing tendency with HF. Two essentially different radiochemical procedures for Pa isolation, differing both in method of initial opening up of the samples and in subsequent cycles of purification, are described in detail. R. A. HOWIE

4721. **Determination of aluminium in thorium oxide and a separation scheme for interfering ions.** G. Goldstein, D. L. Manning and O. Menis (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Talanta*, 1959, **2** (1), 52–60.—Aluminium (0·5 to 150 $\mu$g) in impure thorium oxide is isolated by removing Th, Fe and *Zr* with thenoyltrifluoroacetone (**I**) and then extracting the Al with 8-hydroxyquinoline in $CHCl_3$ in the presence of $H_2O_2$, NaCN and nitrilotriacetic acid. *Procedure*—Dissolve the sample (0·1 g) in boiling $HNO_3$ (1:1) (20 ml) containing a little HF. Add $HClO_4$ (72%) (3 ml) and evaporate to fumes. Cool, add $H_2O$ (5 ml) and ammonium acetate soln. (50%) (8 ml) and adjust to pH 1·5 with $HClO_4$. Dilute to 25 ml with $H_2O$ and extract twice with a 0·5 *M* soln. of **I** in *iso*butyl methyl ketone (10 ml) and wash once with the ketone (10 ml). Dilute the aq. phase to 75 ml, add nitrilotriacetic acid soln. (0·2 *M*) (5 ml), $H_2O_2$ soln. (3%) (2 ml), acetate buffer (200 g of ammonium acetate and 70 ml of conc. aq. $NH_3$ in 1 litre) (2 ml) and 8-hydroxyquinoline soln. (2%) (2 ml). Adjust to pH 8 with aq. $NH_3$ (1:1) and extract twice with $CHCl_3$ (20 ml). Combine the $CHCl_3$ extracts, dilute to 50 ml with $CHCl_3$ and dry with anhyd. $Na_2SO_4$. For $\geqslant$ 10 $\mu$g of Al measure the fluorescence intensity in a spectrophotometer with a fluorescence attachment. For 10 to 150 $\mu$g, measure the extinction at 390 m$\mu$. Slightly modified procedures are necessary for samples containing Ni, Zn, Cd, Mn and Co. The spectrophotometric method gives a coeff. of variation of $\simeq \pm 3\%$ and the fluorescence method $\simeq \pm 5\%$.

W. T. CARTER

4722. **Effect of the mode of combustion on nitrogen determination by Kjeldahl's method.** L. Rozental (Med. Acad., Warsaw). *Roczn. Zakl. Hig., Warszawa*, 1958, **9**, 183–197.—Of the catalysts studied (HgO, selenium metal and $CuSO_4.5H_2O$), yellow HgO proved to be the best. Mixed catalysts saved some combustion time, but the values obtained were lower than for HgO alone. The addition of oxidising agents resulted in a further loss of N. The optimum concn. of $K_2SO_4$ was found to be 7·5 g per 20 ml of $H_2SO_4$ and that of HgO was found to be 1 g per flask.

CHEM. ABSTR.

4723. **Chromatographic separation and microanalysis of nitrogen and nitric oxide in mixtures of nitrogen and oxides of nitrogen using an adsorption column.** M. Lefort and X. Tarrago (Lab. de Phys. Nucléaire, Fac. des Sci. de Paris à Orsay, France). *J. Chromatography*, 1959, **2** (2), 218–220 (in French).—Oxygen, N and NO can be separated on a 3·2-metre column of Linde Molecular Sieve 5A at 84°, with H as carrier gas; 0·010 to 0·500 ml of O or N can be determined with a precision of $\pm$ 0·004 ml. Nitric oxide is not completely eluted and the column must be conditioned with NO before use in order to obtain quant. results. For this component the precision is $\pm$ 0·020 ml in the range 0·050 to 0·150 ml, and $\pm$ 0·006 ml in the range 0·150 to 0·500 ml; $N_2O$ does not interfere. W. T. CARTER

4724. **Determination of water and aniline in hydrazine by infra-red spectrometry.** F. Lalanne (Office Nat. Ind. de l'Azote). *Chim. Anal.*, 1959, **41** (2), 45–48.—Preliminary investigations were carried out on the analysis of hydrazine - $H_2O$ mixtures by the method of Cordes and Tait (*Anal. Chem.*, 1957, **29**, 485) and the analysis of hydrazine - aniline mixtures by differential absorption between 6·4 and 7·4 $\mu$. It is concluded that the presence of up to 2% of aniline leads to an error of 0·4% in the determination of $H_2O$ by the Cordes and Tait method; that the extinction at 6·66 $\mu$ varies with the $H_2O$ content of hydrazine - aniline mixtures from 1 to 6% of $H_2O$, but the difference between the extinctions of the max. at 6·66 $\mu$ and the

min. at 6·5 $\mu$ is independent of the $H_2O$ content for a given aniline content; and that the extinction of the min. at 7·15 $\mu$ is proportional to the $H_2O$ content for values < 7%. Two methods have been developed for the complete analysis of ternary hydrazine mixtures containing < 10% of $H_2O$ and aniline. (*i*) Aniline is determined by measuring the difference in the extinctions at 6·5 $\mu$ and 6·66 $\mu$, and $H_2O$ by the Cordes and Tait method with the addition of a correction of 0·2% for each 1% of aniline. The method gives an absolute accuracy of 0·05% for aniline and 0·1% for $H_2O$ in the concn. range 0 to 2·5% of aniline. Disadvantages are that two series of measurements and relatively large samples are necessary. (*ii*) Aniline and $H_2O$ are determined simultaneously by measuring the differential absorption curves of the mixture against pure hydrazine between 6·4 and 7·4 $\mu$, the $H_2O$ content being determined by the absorption at 7·15 $\mu$ and the aniline content as in method (*i*). The accuracy is 0·05% for both aniline and $H_2O$ for the concn. range 0 to 2·5% of aniline and 0 to 7% of $H_2O$. S. M. MARSH

4725. **Colorimetric determination of nitrite with NNN′N′-tetramethylbenzidine.** M. Matrka and F. Navrátil (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Průmysl*, 1959, **9** (2), 75–76.—NNN′N′-Tetramethylbenzidine (**I**) reacts with nitrite in an acid medium yielding the orange NN′-dimethyldiphenoquinonedi-imine dimetho-chloride which can be determined photometrically. *Calibration curve*—To the soln. of **I** (0·1% in *N* HCl) (1 ml) add *N* HCl (9 ml) and 0·5 to 3 ml of aq. nitrite soln. (0·01 g of $NaNO_2$ per litre). After 15 min. dilute to 100 ml and after 3 hr. measure the extinction at 475 m$\mu$. The mechanism of the reaction has been studied by means of the colorimetric titration of $10^{-4}$ *M* **I** with $10^{-3}$ *M* $NaNO_2$. Dichromate, $MnO_4^-$, $Ce^{4+}$, $SO_3^{2-}$ and $S_2O_4^{2-}$ interfere. This reaction can also be used for the colorimetric determination of strongly oxidising agents (*e.g.*, Cl, Br and chromates). J. ZÝKA

4726. **Rapid determination of phosphorus in coal and coke.** I. I. Édel'man, L. S. Zabora and N. D. Khizhnyak (Ukraine Sci. Res. Coal Chemistry Inst.). *Zavod. Lab.*, 1959, **25** (2), 159–160.—The sample (1 g of coal or 0·5 g of coke) is ashed at 850° with free access of air and the residue is dissolved in 10 ml of a mixture of $H_2SO_4$ and $HNO_3$ (2:1). Two aliquots (25 ml) of the filtered and diluted soln. (100 ml) are treated at 50° to 60° with 4 ml of a soln. of $Fe^{3+}$ [108 g of $(NH_4)_2SO_4.Fe_2(SO_4)_3$ in 300 to 350 ml of water] and 5 ml of conc. HCl. Each soln. is diluted to 500 ml and treated with aq. $NH_3$ and 4 *N* HCl so that there is a 2-ml excess of the acid. The soln. are boiled for 1 min. with 5 ml of 20% $Na_2SO_3$ to decolorise. More $Na_2SO_3$ is added if necessary to reduce all the $Fe^{3+}$. If a gold-coloured tint appears, a few drops of 4 *N* HCl are added. The cooled soln. are then treated with 6 ml of 4 *N* HCl and one of them is treated with 4 ml of 5% $(NH_4)_2MoO_4$ soln., the other soln. serving as a control. The colour intensity is measured with a red filter, and the content of P is calculated from a calibration curve. G. S. SMITH

4727. **Examination of oxy acids of phosphorus by electrochromatography.** Takuya R. Sato (Argonne National Lab., Lemont, Ill., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 841–845.—The extension of the distance of differential electrical migration by the use of filter-paper moistened with 0·1 *M* acetic acid permits the separation of slow migrants in mixtures of complex and condensed phosphorus oxy acids. The separation is also aided by variations in the electrolyte and by the addition of reagents (*e.g.*, $Zn^{2+}$) in zones retaining certain components only. The d.c. potential is either 5 or 10 to 15 V per cm (for 17 to 20 and 2 to 4 hr., respectively). The resolved zones are located by spraying with molybdate, neutron activation (and scanning), or autoradiography. The sequence and separability are established for $Na_2HPO_4$, $Na_2HPO_3$, $NaH_2PO_2$, $Na_4P_2O_7$, $Na_5P_3O_{10}$, $(NaPO_3)_3$, $(NaPO_3)_4$, $Na_3HP_2O_6$, $Na_2HP_2O_5$, $Na_2H_2P_2O_5$ and $Na_2H_2P_2O_6$. The sensitivity of the method is very high (approx. $10^{-9}$ g for non-radioactive phosphorus compounds). The method is suitable for the examination of irradiated natural products and the purity and deterioration of standard prep., and for the purification of tracers. J. P. STERN

4728. **Simultaneous titrations of antimony and arsenic with the dead-stop end-point.** Nan-Sun Young, T'sing-Chuan Tien and Sheau-Shya Kao (Chem. Dept., Peking Univ.). *Acta Chim. Sinica*, 1959, **25** (2), 106–109.—The dead-stop end-point method is applied to the determination of Sb and As in anode mud without previous separation, standard $Ce(SO_4)_2$ soln. being used as the titrant. The sample is dissolved in conc. $H_2SO_4$. The digest is diluted with water and adjusted to 6 *N* in HCl; $Sb^{5+}$ are titrated with 0·1 *M* $Ce(SO_4)_2$ at an applied voltage of 60 mV at 0°, at which temp. the $Sb^{3+}$ - $Sb^{5+}$ system is reversible. The soln. is then adjusted to 4 *N* in HCl and warmed to 15° to 22°, ICl soln. being added to render the $As^{3+}$ - $As^{5+}$ system reversible. The titration is continued until $As^{3+}$ are completely oxidised. A complete analysis takes ≃ 3 hr. Satisfactory results for Sb and As in two samples of anode mud are reported. S. H. YUEN

4729. **New colorimetric method for the determination of tervalent antimony in the presence of tervalent arsenic.** D. G. Constantinescu, G. Baiulescu and R. Oteleanu (Parhon Univ.). *Acad. R.P.R., Stud. Cercet. Chim.*, 1959, **6** (3), 439–444.—The method is based on the reaction of a methanolic soln. of antimony and arsenic chlorides with a methanolic soln. of quercetin (0·05%), the resulting yellow colour being measured in the 1-cm cell of a Pulfrich photometer with a S42 filter. From 1·37 to 10·98 $\mu$g of Sb per ml can be determined. Arsenic does not interfere unless its concn. is more than six times that of the Sb. H. SHER

4730. **Rapid methods of determining antimony in bronze.** R. S. Volodarskaya. *Zavod. Lab.*, 1959, **25** (2), 143–144.—Methods based on the iodide and the thiourea complexes are described. With the former, 0·1 g of sample is heated with 5 ml of water and 10 ml of conc. $H_2SO_4$ and the cooled soln. is mixed with 50 ml of water and then diluted to 100 ml with dil. $H_2SO_4$ (1:5). An aliquot (10 ml) is mixed with 30 ml of dil. $H_2SO_4$ (1:5), 10 ml of 10% thiourea soln. and 20 ml of 10% KI soln. and then diluted to 100 ml with dil. $H_2SO_4$ (1:5). After 8 to 10 min. the extinction is measured with a violet or blue filter, and the content of Sb is found by means of a calibration curve. With the thiourea method, 0·1 g is dissolved in 5 ml of water and 10 ml of conc. $H_2SO_4$, and the soln. is evaporated to fuming, then diluted with water (20 ml), treated with 60 ml of 10% thiourea soln., and diluted to 100 ml with dil. $H_2SO_4$ (1:5). The

extinction is measured after 5 to 7 min., but within 20 min., after the addition of thiourea. A violet or blue filter is used. The methods are suitable for contents of Sb from 0·1 to 7%. G. S. SMITH

4731. **Spectrographic analysis of antimonate, stannate and products obtained during their treatment.** I. G. Yudelevich, F. P. Polatbekov and V. G. Kovaleva (S. M. Kirov Kazakh State Univ.). *Zavod. Lab.*, 1959, **25** (3), 305–307.—Conditions for the spectrographic determination of Sn, Cu, Pb, Fe, As, Al, Te and In in antimonate, and of Sb, Fe, Cu, As, Pb, Te and In in stannate, and for the analysis of metallic tin and antimony, etc., are described. G. S. SMITH

4732. **Spectrographic analysis of antimony and antimony sulphide for heavy metals.** G. F. G. Knipe (Res. Dept., African Explosives & Chem. Industries, Ltd., P.O. Northrand, Transvaal). *Spectrochim. Acta*, 1959, (1), 49–55.—A spectrographic method is described for the determination of As, Cu, Fe and Pb in the range 0·01 to 1·0% in metallic antimony. The sample is first converted into the oxide by treatment with conc. $HNO_3$, then compared with synthetic standards by arcing to completion in an 8-amp. d.c. arc. The same elements, together with Bi and Zn, are determined in antimony sulphide by a similar technique. Spectra are evaluated by means of a "Respektra" calculating board; coeff. of variation between 5 and 10% are claimed. P. T. BEALE

4733. **Photometric determination of bismuth with tetraphenylphosphonium bromide.** Nobusiha Matano and Akira Kawase. *Trans. Nat. Res. Inst. Met., Japan*, 1959, **1** (1), 69–71 (in English).—A rapid method for determining Bi is based on the pptn. of orange tetraphenylphosphonium tetraiodobismuthate, which is sol. in $CHCl_3$. *Procedure*—To the sample soln. (> 120 μg of Bi) are added 3 ml of 1% KI soln., 5 drops of phenylhydrazine soln. (1% in dil. $H_2SO_4$) and 3 ml of 0·01 *M* aq. tetraphenylphosphonium bromide. The mixture, which should be $\simeq 2$ *N* in $H_2SO_4$, is set aside for 10 min., and then extracted with $CHCl_3$. After separation, the organic layer is filtered through a cotton pad into a 1-cm cell, and its extinction is measured against that of a $CHCl_3$ blank at 505 mμ. Interference is shown by $Fe^{3+}$, $Cu^{2+}$, $Hg^{2+}$, $Cd^{2+}$, $Sn^{2+}$ and $Sn^{4+}$; that due to $Sb^{3+}$ is eliminated by the addition of K Na tartrate. Beer's law is obeyed up to 120 μg of Bi. J. H. WATON

4734. **Complexometric method of determining bismuth in multi-component alloys [of bismuth, lead, cadmium and tin].** A. I. Cherkesov and A. S. Mel'nikova (Astrakhan Tech. Inst. of the Fishing Industry). *Zavod. Lab.*, 1959, **25** (2), 140–141.—The alloy (0·2 to 0·4 g) is dissolved in 10 to 15 ml of dil. $HNO_3$ (1:1) and the cooled soln. is diluted to 500 ml. An aliquot (10 ml) of the well-shaken soln. (some of the Bi is adsorbed on the insoluble metastannic acid) is treated with 5 drops of a 1% ethanolic soln. of haematoxylin, and titrated with 0·001 *M* EDTA until the colour changes from violet to pale yellow. The soln. is then vigorously shaken, the violet colour reappearing, and the titration is continued. Shaking and titration are continued until all the Bi has been desorbed. If the sample contains from 4 to 15% of Sb, the soln. to be titrated is first mixed with 0·5 ml of saturated NaF soln. Gallein can be used as indicator instead of haematoxylin, but the colour change at the end-point is somewhat less sharp. G. S. SMITH

4735. **Spectrophotometric and photometric microdetermination of vanadium.** F. Bermejo Martínez and M. Paz Castro (Lab. of Anal. Chem., Fac. of Sci., Univ. of Santiago de Compostela, Spain). *Chemist Analyst*, 1959, **48** (1), 2–3.—Acid soln. of $VO^{2+}$ give an intense colour with $H_2O_2$ and 1:2-di-(2-aminoethoxy)ethane-NN′-tetra-acetic acid (EGTA) (**I**). The test soln. (> 120 μg of V) is treated with 2 ml of 5% aq. soln. of **I** (disodium salt), 10 ml of Clark and Lubs buffer soln. (pH 1·70) and 1 ml of 30% $H_2O_2$ soln. The pH is adjusted to 1·70 (pH meter) and the mixture diluted to 25 ml. After 25 min. the absorption is read spectrophotometrically at 426 mμ or photometrically with an Ilford No. 601 filter, in a 1-cm cell, and results are referred to the appropriate calibration curve. Very high concentrations of $Fe^{III}$, $Ti^{III}$, $Cu^{II}$, $U^{VI}$, $Mo^{VI}$ and $W^{VI}$ interfere, but moderate amounts of Fe and Ti can be masked with fluoride. Moderate amounts of other metals, minor amounts of $W^{VI}$, and $SO_4^{2-}$, $PO_4^{3-}$, $NO_3^-$, $Br^-$, $Cl^-$, $NH_4^+$, $K^+$ and $Na^+$ do not interfere, so that a variety of reagents can be used for dissolution of the sample and adjustment of pH. Owing to the limited interferences, microgram amounts of V can be determined in complex materials. R. E. ESSERY

4736. **Method for the spectrographic determination of trace impurities in niobium.** D. E. Fornwalt and M. K. Healy (Pratt & Whitney Aircraft Div., CANEL Operations, Middletown, Conn., U.S.A..) *Appl. Spectroscopy*, 1959, **13** (2), 38–40.—The method described involves the conversion of Nb into the oxide by heating in platinum at 800°. A 10-mg sample plus 10 mg of $Li_2CO_3$ as a spectrographic buffer and 25 μg of La as internal standard is excited in a 20-amp. d.c. arc. The spectrogram obtained can be used to determine Cd, Cr, Co, Fe, Mn, Mo, Ni, Sn and Ti in the 0·001 to 0·1% concn. range. A separate 20-mg sample is excited to determine B (0·0001 to 0·0015%), Al and Si (0·001 to 0·1%), Ta (0·025 to 1·5%) and Zr (0·001 to 1·5%). The coeff. of variation ranged from 2% for Zr to 19% for Sn. K. A. PROCTOR

4737. **Chemistry of niobium and tantalum. XIX. Separation of niobium and tantalum.** H. Schäfer (Anorg.-Chem. Inst. d. Univ., Münster, Westphalia, Germany). *Angew. Chem.*, 1959, **71** (4), 153–160.—A review is given of procedures for the separation of Ta and Nb, subdivided under three main headings —fractionation of compounds based on differences in physical properties; separations based on reduction of $Nb^V$; and separations based on differences in stability towards hydrolysis (including ion-exchange techniques). (134 references.) T. R. ANDREW

4738. **Photometric determination of tantalum with phenylfluorone.** C. L. Luke (Bell Telephone Lab. Inc., Murray Hill, N.J., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 904–906.—Tantalum forms a red complex with 2:3:7-trihydroxy-9-phenyl-6-fluorone (**I**) suitable for photometry at 530 mμ. Interference by other metals is avoided by extracting Ta from an HF - HCl soln. with *iso*butyl methyl ketone (**II**) and masking any co-extracted metals with EDTA (disodium salt) (**III**). For satisfactory accuracy (not defined), the pH and the concn. of $F^-$, **I**, **III** and buffer must be closely controlled. *Procedure*—Dissolve the dry sample (free from

$SO_4^{2-}$, $ClO_4^-$ or $Cr^{VI}$) in 5 ml of acid (5 ml of HF, 5 ml of HCl and 90 ml of $H_2O$), cool, and extract with **II** (2 × 5 ml). Separate and evaporate the organic phase. Add $HClO_4$ (0·25 ml) and $HNO_3$ (0·25 ml) and heat until $HClO_4$ is copiously evolved. Add $HNO_3$ (0·25 ml) and evaporate to dryness. Cool, add 1 ml of HF (1:99) and warm until dissolution is complete. Add 5 ml of 10% aq. **III**, 10 ml of ammonium acetate - acetic acid buffer (pH 4·5) and 10 ml of 0·01% **I** in 10% methanol, and set aside for 30 min. Add 5 ml of satd. $H_3BO_3$ soln. (corrosion inhibitor), make up to 50 ml with acetic acid (1:9), and immediately determine the extinction at 530 mμ. Read the Ta content from a calibration curve. J. P. STERN

4739. **Spectrographic determination of micro amounts of titanium, niobium and tantalum.** T. M. Moroshkina and V. K. Prokof'ev. *Vestn. Leningr. Univ.*, 1959, No. 10, *Ser. Fiz. i Khim.*, (2), 143–148.—The following lines were used in the determinations—Ti 4305·92 A, Nb 2927·81 A, Ta 2933·55 A, Nb 2950·88 A, and Ta 2951·9 A. Uranium (4297·11 A) or Cr (4297·73 A) was used as an internal standard in the determination of Ti, Ta in the determination of Nb, and Nb in the determination of Ta; Fe (2929·01 A) was used as the comparison element in the determination of Nb and Ta. Spectra were excited in a stabilised a.c. arc at 220 V and a current of 7 to 8 amp. for the determination of Ti and a current of 20 amp. for Ta and Nb. The admixture (prepared by fusing the oxide of Ti, Nb or Ta with $K_2S_2O_7$ and dissolving the product in conc. $H_2SO_4$) and the internal standard soln. are added to the sample, which is ignited at 700° for 20 to 25 min. and then placed in the bore of a carbon electrode. The results showed that the direct spectrographic determination of small amounts of Ti in natural samples of complex composition with evaporation of the sample from a bead and with the admixture method presents no difficulties; Ti was determined in the range 5 × $10^{-4}$ to 0·5% with an accuracy of ±10%. The simultaneous determination of Nb and Ta can be carried out for a range of 0·01 to 1%; with lower concn. of Nb and Ta, the determination can be carried out with ratios of Nb to Ta of 1:1 to 1:2. K. R. C.

4740. **Paper electrophoresis of protactinium(V).** J. Vernois (Inst. du Radium, Paris, France). *J. Chromatography*, 1959, **2** (2), 155–161 (in French).—The behaviour of $Pa^V$, $Fe^{III}$, $UV^I$, $Pb^{IV}$, $Bi^{III}$, $Zr^{IV}$, $Ta^V$, $Nb^V$, $Ti^{IV}$, $Th^{IV}$ and $Po^{III}$ has been studied with HF and mixtures of HCl and HF as electrolytes and a potential difference of 150 V. Protactinium can be separated from Zr, Ti, Th and Fe, and Zr can also be separated from Nb. W. T. CARTER

4741. **Separate determination of peroxide oxygen and superoxide oxygen in superoxides.** I. V. Vol'nov and E. I. Latysheva (Kurnakov Inst. Gen. and Inorg. Chem., Acad. Sci., Moscow). *Zhur. Anal. Khim.*, 1959, **14** (2), 242–243.—In the analysis of materials containing peroxides and superoxides, the gasometric determination of peroxide oxygen can be satisfactorily replaced by a permanganate titration (0·1 *N* $KMnO_4$) of the peroxide oxygen formed in acetic acid soln. during the gasometric determination of superoxide oxygen by the method of Seyb and Kleinberg (*Anal. Chem.*, 1951, **23**, 115); the presence of diethyl phthalate in the soln. does not affect the titration. K. R. C.

4742. **Determination of small amounts of hydrogen in sulphur. Application to the determination of water in the presence of sulphur trioxide.** G. Barrier (Lab. d'Essais des Prod. Chim., Comp. de Saint-Gobain, Chauny et Cirey, Aubervilliers, France). *Chim. Anal.*, 1959, **41** (3), 97–104.—Different types of organic matter present in sulphur are discussed and three methods for the determination of H are described. *Determination of H by combustion*—The $SO_3$ and $SO_2$ formed by combustion of S are absorbed on $Na_2CO_3$ - $CaSO_4$, and the $H_2O$ is absorbed with anhydrone. Apparatus and procedure are described. The method is not subject to systematic error. If sulphur is replaced with $H_2SO_4$, the $H_2O$ content of the acid may be similarly determined, but more precisely than by titration. *Determination of humidity in gases containing $SO_3$*—A simple furnace is described for fixing $SO_3$ as before. *Determination of H by thermal cracking*—The sample of sulphur is heated at the b.p. for 1 hr. under an inert gas, and the $H_2S$ evolved is absorbed in Zn or Cd acetate soln.; the determination is completed iodimetrically. The method is rapid, and sufficiently accurate (80 to 90% recovery of H) to serve for the control of S purification. Moisture does not interfere. P. D. PARR-RICHARD

4743. **Solubility of hydrogen sulphide in water.** R. Belcher and J. P. G. Farr (Dept. of Chem., Univ., Edgbaston, Birmingham, England). *Talanta*, 1959, **2** (1), 95–97.—The $H_2S$ generated from ferrous sulphide and HCl (1:1) contains large amounts of hydrogen. A generator which had been working for several hours produced gas containing ≃ 80% (v/v) of $H_2S$, but after shutting down for 18 hr. the concn. of $H_2S$ fell to 50% (v/v). The purity of the $H_2S$ increases with increase in the rate of generation. Only rarely were soln. 0·05 *M* in $H_2S$ produced at room temp. under conditions comparable to those existing in qual. analysis. This must be taken into account in mass-action calculations concerned with the pptn. of sulphides. W. T. CARTER

4744. **The sulphur acids. XVI. Iodimetric and colorimetric determination of sulphanes [hydrogen polysulphides], elementary sulphur and sulphane - sulphur mixtures.** M. Schmidt and G. Talsky (Inst. f. Anorg. Chem. d. Univ., München). *Z. anal. Chem.*, 1959, **166** (4), 274–283.—Hydrogen polysulphides ($H_2S_x$) react with $Na_2SO_3$ to give $H_2S$ and $Na_2S_2O_3$, according to the equation—$H_2S_x + (x-1)SO_3^{2-} \rightarrow H_2S + (x-1)S_2O_3^{2-}$. The $H_2S$ is absorbed in a soln. of $Zn^{2+}$ or $Cd^{2+}$ and titrated, and, after addition of formaldehyde to react with the excess of $SO_3^{2-}$, the $S_2O_3^{2-}$ are determined. In homogeneous soln. S may be determined from the reaction $S_8 + 8SO_3^{2-} \rightarrow 8S_2O_3^{2-}$. Details of the procedure for polysulphides, sulphur and for mixtures are given. Photometric procedures have been developed based on the formation of $SCN^-$, by reaction with $CN^-$, and measurement of the colour produced with $Fe^{3+}$. A scheme of application for inorganic sulphur compounds that can be converted into sulphides or sulphur, and for organic sulphur compounds is given. T. R. ANDREW

4745. **Determination of inorganic sulphur compounds in sulphate black liquor. I. Determination of thiosulphate and sulphite by potentiometric titration with mercuric chloride.** E. Bilberg (The Norwegian Pulp and Paper Res. Inst., Oslo). *Norsk Skogind.*, 1958, **12** (11), 470–478 (in

English).—Sulphite and $S_2O_3^{2-}$ can be titrated potentiometrically in the presence of $S^{2-}$ which give a wave well separated from that due to $S_2O_3^{2-}$. Sulphate, $CO_3^{2-}$, $PO_4^{3-}$ and acetate do not interfere; $I^-$ and $SCN^-$ must be absent; $Cl^-$ affect the sharpness of the end-point. A mercury pool connected through a platinum electrode is used as the indicator electrode; potentials are measured *vs.* the S.C.E. *Procedure for sulphite plus thiosulphate*—Add an aliquot containing 0·025 to 0·25 g of $Na_2S_2O_3$ and 0·02 to 0·2 g of $Na_2SO_3$ to the titration beaker and dilute to 100 ml with air-free $H_2O$. Add 5 ml of glycerol and adjust the pH to between 7·0 and 7·5. Titrate with 0·05 *M* $HgCl_2$. *Procedure for thiosulphate*—Make another aliquot up to 100 ml, adjust the pH to between 7·0 and 7·5, add 5 ml of 40% formaldehyde soln. and set aside for 5 min. before titrating. For the determination of $SO_3^{2-}$ and $S_2O_3^{2-}$ in black liquor, it is better to precipitate $S^{2-}$ with a suspension of $CdCO_3$, filter off the CdS and titrate under N. The precision for the $SO_3^{2-}$ determination is less than that of iodimetry; that for $S_2O_3^{2-}$ is as good. P. D. PARR-RICHARD

4746. **Analytical applications of oxidations with ferricyanide catalysed with osmium tetroxide. III. Simultaneous determination of sulphur compounds.** F. Solymosi and A. Varga (Inst. for Inorg. and Anal. Chem., Sci. Univ. of Szeged, Hungary). *Magyar Kém. Foly.*, 1959, **65** (2), 52–55.—For the simultaneous determination of $S_2O_4^{2-}$ and $SO_3^{2-}$ or $S_2O_4^{2-}$ and $S_2O_3^{2-}$, oxidise $S_2O_4^{2-}$ to $SO_3^{2-}$ with $Fe(CN)_6^{3-}$ (**I**) in a 0·5 to 1 *N* NaOH soln. After the end-point, increase the alkalinity to 4 to 4·5 *N*, add $OsO_4$ soln. (**II**) (2 to 3 drops), heat at 50° to 60°, and complete the titration to oxidise $SO_3^{2-}$ and $S_2O_3^{2-}$ to $SO_4^{2-}$. The first titration (*a* ml) gives the concn. of $S_2O_4^{2-}$ directly; from the second (*b* ml) that of $SO_3^{2-}$ or $S_2O_3^{2-}$ can be calculated as ($b - 2a$). Unless the titrations are rapid, a nitrogen atmosphere is recommended; the end-point can be determined by the dead-stop method or potentiometrically. To determine $S_2O_4^{2-}$, $SO_3^{2-}$ and $S_2O_3^{2-}$, titrate $S_2O_4^{2-}$ in a 0·5 to 1 *N* NaOH soln. (*a* ml); then determine $SO_3^{2-}$ plus $S_2O_3^{2-}$ at the higher pH as above (*b* ml). Oxidise the next aliquot with an excess of iodine in weakly acid soln. to $SO_4^{2-}$ and $S_4O_6^{2-}$; remove the excess of iodine with $SO_3^{2-}$ and titrate the $S_4O_6^{2-}$ (which are formed from $S_2O_3^{2-}$) in 5 *N* NaOH with **I** in the presence of **II** at 50° (*c* ml). All end-points are determined by the dead-stop method. From the three titrations, the concn. can be calculated—1 ml of 0·1 *M* **I** ≡ 8·70 mg of $Na_2S_2O_4$ (from titration *a*) or 6·30 mg of $Na_2SO_3$ (from titration *b*) or 1·97 mg of $Na_2S_2O_3$ (from *c*). The accuracy is within 0·4%. The simultaneous determination of $SO_3^{2-}$ and $S_2O_3^{2-}$ is accomplished by oxidising the first aliquot in 4 to 4·5 *N* NaOH at 50° with **I** (*d* ml) in the presence of **II** and the second aliquot with iodine as already described (*e* ml). The concn. of $SO_3^{2-}$ is calculated from ($d - 8e/7$) and that of $S_2O_3^{2-}$ is $8e/7$. To determine $S_2O_3^{2-}$ and $S_4O_6^{2-}$ simultaneously, oxidise both to $SO_4^{2-}$ with **I** in 5 *N* NaOH (*f* ml) in the presence of **II**. Oxidise the second aliquot with iodine in weak acid; $S_2O_3^{2-}$ give $S_4O_6^{2-}$; titrate this with **I** (*g* ml). The wt. of $S_2O_3^{2-}$ is $f - g/8$ and that of $S_4O_6^{2-}$ is $f - (f - g)/8$. A. G. PETO

4747. **Colorimetric determination of thiosulphate in the presence of polythionates and hydrogen sulphite.** N.-H. Schöön (Dept. of Engng Chem., Chalmers Tekniska Högskola, Göteborg, Sweden). *Acta Chem. Scand.*, 1959, **13** (3), 525–532 (in English).—The AgSCN method of Schöön (*cf. Anal. Abstr.*, 1959, **6**, 2117) gives erroneous results in the presence of polythionates and $H_2SO_3$. A new but less sensitive method is described in which thiosulphate is caused to react with *p*-benzoquinone in acetic acid soln., and the resulting colour is measured absorptiometrically. Polythionates do not interfere and interference from $H_2SO_3$ can be completely suppressed by the addition of excess of formaldehyde. The method is applicable to concn. of $S_2O_3^{2-}$ in the range 0·03 to 0·3 m*M*. W. T. CARTER

4748. **Plasmoquin [pamaquin] as a reagent in inorganic analysis. I. Detection of chromium(VI).** Te-Fung Lee, Nai-Ching Wang and Nai-Kuei Shen. *Acta Chim. Sinica*, 1958, **24** (6), 403–406.—Pamaquin in the presence of 0·1 *N* $HClO_4$ and 8% oxalic acid reacts with $CrO_4^{2-}$ (or $Cr_2O_7^{2-}$) to give a red - violet colouration which is not extracted by ordinary organic solvents. The limit of identification is 0·05 μg at a dilution limit of 1 in $1 \times 10^6$. Quadrivalent Ce, $Au^{3+}$, $VO_3^-$, $BrO_3^-$, $IO_3^-$, $IO_4^-$ and $NO_2^-$ interfere with the detection of $CrO_4^{2-}$. Of the interfering ions, $Ce^{4+}$ and $Au^{3+}$ can be separated by aq. $NH_3$, and $VO_3^-$ by 8-hydroxyquinoline - $CHCl_3$ extraction. In a mixture containing $Ce^{4+}$, $Au^{3+}$, $VO_3^-$ and $Cr^{3+}$ in concn. up to 20:20:20:1, $Cr^{3+}$ (0·009 μg per 0·05 ml) can still be detected. Chromium should be previously oxidised in $H_2SO_4$ soln. with $(NH_4)_2S_2O_8$ or in alkaline soln. with $H_2O_2$ before separation of the ions. SCI. ABSTR. CHINA

4749. **New method for determination of molybdenum.** F. da Silva and L. de Moura (Inst. Sup. Técnico, Lisbon, Portugal). *Técnica*, 1959, **34** 437–443.—Conditions for the colorimetric determination of Mo with diphenylcarbazone have been studied and the following procedure is proposed. To 1 ml of the soln. (containing ≃25 μg of $Mo^{6+}$) is added 1 ml of 0·1 *N* $H_2SO_4$, and after 1 min. the mixture is extracted for 30 sec. with 10 ml of a soln. (0·0025 *M*) of diphenylcarbazone in *iso*amyl acetate. After 5 min. the organic phase is separated, then centrifuged for 2 min., and the extinction at 540 mμ is measured. A blank is carried out with the reagent and the concn. of $Mo^{6+}$ is derived from a calibration graph. If V is present, the pH is lowered by using more concentrated (0·5 *N*) $H_2SO_4$. The use of the method for special steels is described; modifications are necessary if W is present. L. A. O'NEILL

4750. **Volumetric determination of tungsten in its minerals.** L. Perrier (Comp. Ind. des Metaux Electroniques, Saint Pierre-de-Rumilly, Haute-Savoie, France). *Bull. Soc. Chim. France*, 1959, **26** (1), 177.—*Procedure*—The mineral (2·5 to 3·0 g) is ground, sieved and roasted and fused for 1 hr. with 12 g of $Na_2CO_3$ - $K_2CO_3$, and dissolved in < 150 ml of water. Manganese is oxidised by boiling with $H_2O_2$. The soln. is filtered into a 250-ml flask, and the filtrate and washings are made up to vol. A 50-ml aliquot is neutralised to methyl orange with aq. $H_2SO_4$ (1:2), and 5 ml of $H_3PO_4$ (*d* 1·71) and 10 ml of aq. $H_2SO_4$ (1:2) are added. The soln. and rinsings are poured into a Jones reductor prepared according to Charlot and Bezier (*"Analyse Quantitative Minérale,"* Masson, 1955, 3rd Ed., p. 590), and after exactly 30 min. are run into 40 ml of 10% $(NH_4)_2SO_4.Fe_2(SO_4)_3$ soln. and 4 ml of $H_3PO_4$ (*d* 1·71). The column is washed

out into the flask and the contents are titrated with 0·1 *N* $KMnO_4$. Molybdenum and V, if present, interfere. E. J. H. Birch

4751. **Determination of the solubility of barium tungstate by means of the radioactive isotope tungsten-185.** I. E. Zimakov (State Sci. Res. Inst. of Non-Ferrous Metals). *Zavod. Lab.*, 1959, **25** (2), 133–134.—The solubility (in mg of W per 100 ml) of $BaWO_4$ in water is 0·729 at 0°, 0·650 at 4°, 0·641 at 10°, and 1·522 at 99°. The solubility *vs.* temp. curve is almost linear from 10° to 99°. The effect of changes of pH (by the use of HCl and NaOH) is shown graphically. The min. solubility is at pH 6 to 7 and this is accordingly the best pH for the separation of W and Re. G. S. Smith

4752. **Application of ion exchange to the colorimetric determination of trace amounts of uranium using dibenzoylmethane.** H. J. Seim, R. J. Morris and R. G. Pastorino (Univ. of Nevada, Reno, U.S.A.). *Anal. Chem.*, 1959, **31** (5), 957–958.—After purification on anion exchangers (*cf.* Seim *et al.*, *Anal. Abstr.*, 1957, **4**, 2969), U is complexed with dibenzoylmethane (**I**) in 80% ethanol and determined colorimetrically at 400 mμ. The method is suitable for the routine determination of U in ores, interference by Th and $Ca_3(PO_4)_2$ being minimised by a double column-adsorption. For U contents of 0·01 to 0·1%, the average deviation is ≯ 0·002%. *Procedure*—Completely free the eluate from the anion exchanger, containing the U, from $HClO_4$ by evaporation and heating at 250° to 300° for 10 to 20 min. Cool, add water (10 ml) and 95% ethanol (25 ml), and a 1% ethanolic soln. of **I** (1 ml) Bring to pH 7·0 to 7·5 with 0·005 *M* NaOH or $H_2SO_4$, dilute to 50 ml with 95% ethanol, filter, and measure the extinction at 400 mμ against a blank (1 ml of 1% **I** soln. in 50 ml of 80% ethanol). J. P. Stern

4753. **Machine for preparing phosphors for the fluorimetric determination of uranium.** R. E. Stevens, W. H. Wood, K. G. Goetz and C. A. Horr (U.S. Geol. Survey, Denver, Colo., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 962–964.—The machine described is designed for use in the procedures of Grimaldi *et al.* (*U.S. Geol. Survey, Circ.* No. 199, 1952). Phosphors prepared during the same run show good reproducibility, and separate runs show good agreement. The operation of the machine requires little skill and phosphors can be prepared three times as rapidly as by hand. K. A. Proctor

4754. **Accurate determination of uranium in the presence of small amounts of molybdenum. Lead reductor and stannous chloride methods.** J. T. Byrne, M. K. Larsen and J. L. Pflug (Rocky Flats Plant, Dow Chemical Co., Denver, Colo., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 942–945.—Low and erratic results are obtained when metallic uranium containing 100 p.p.m. of Mo is analysed by the lead-reductor method after fuming the sample with $HClO_4$, but when the sample is fumed with $H_2SO_4$, Mo (2000 p.p.m.), Fe (1000 p.p.m.) and Si (200 p.p.m.) do not interfere. The interference is attributed to the Mo-catalysed reduction of $ClO_4^-$ by lead, giving a product which oxidises $U^{4+}$. A comparison of the lead-reductor method (fuming with $H_2SO_4$) with the Jones reductor method shows the latter to be unsatisfactory for Mo concn. > 50 p.p.m. Analyses by the $SnCl_2$ method are accurate for concn. of Mo ≯ 6·6% if Mo is determined separately and a correction applied on the basis of a three-electron change for the Mo. There is no interference from Al, Ca, Ni and Zn (2%) in the $SnCl_2$ method, but Cr and Zr cause low results and Cu (2%), Ti, W and V high ones. J. P. Stern

4755. **Spectrophotometric determination of microgram quantities of molybdenum in uranium trioxide using dithiol.** A. W. Ashbrook (Res. and Devel. Div., Eldorado Mining & Refining, Ltd., Ottawa, Ontario, Canada). *Chemist Analyst*, 1959, **48** (1), 5–7.—Dissolve a portion of $UO_3$ containing 2 to 8 μg of Mo in 100 ml of HCl (1:1) with heating. Transfer to a separating-funnel, cool to 30° to 35°. Add 0·2 to 0·3 g of hydrazine sulphate, and shake to dissolve. Add 2 ml of dithiol soln. (0·2% in 1% NaOH soln.), mix, and allow to stand for 10 min. Add 10 ml of $CCl_4$, shake vigorously for 1 min., and allow to separate. Filter the $CCl_4$ layer through a dry paper and measure its extinction in a 1-cm cell at 670 mμ against a $CCl_4$ blank. Refer the results to a calibration curve. Beer's law is obeyed up to 10 μg of Mo. Results for amounts of Mo from 0·1 to 0·26 p.p.m. in high-purity $UO_3$ show good replication. R. E. Essery

4756. **Radiometric analysis of leached uranium-thorium ore samples with the $\beta$-$\gamma$-$\gamma$ method.** P. W. de Lange (National Physical Res. Lab., Pretoria, S. Africa). *Anal. Chem.*, 1959, **31** (5), 812–813.—In this procedure, the ordinary $\beta$-$\gamma$ method calculations are made after the $ThO_2$ concn. has been determined, using the 2·6-MeV $\gamma$-photopeak from $^{208}Tl$. The results obtained by this method agree well with chemical determinations of $U_3O_8$ and $ThO_2$. The minimum concn. which can be determined is 0·1% in an 18-g sample of ore. K. A. Proctor

4757. **Quantitative determination of halogen in a single drop.** H. Ballczo and L. Hainberger (Chem. Inst., Univ., Vienna). *Mikrochim. Acta*, 1959, (3), 466–472.—Fractional pptn. of $I^-$, $Br^-$ and $Cl^-$ (0·05 to 1 micro-equiv. of halide) dissolved in a single drop (0·001 to 0·05 ml) is carried out by placing the drop in the centre of a White Ribbon filter-paper impregnated with Ag oxalate. After suitable development by chemical or photochemical means, the annular zones may be readily differentiated. The areas of the zones are measured and the ratio of these areas to the area of the surface impregnated with Ag oxalate forms the basis of the procedure for determining the absolute amounts of halides in the test drop. The relative accuracy is ±10%. A similar procedure may be used for ensuring the uniform distribution of carrier-free radioactive iodine over a paper area which corresponds to that of the counting tube, thus reducing the error of the counting technique. D. F. Phillips

4758. **Micro-determination of fluorine applicable to atmospheres and to biological media.** R. Fabre, R. Truhaut and J. Bernuchon (Lab. Toxicol. et d'Hygiène Ind., Fac. Pharm., Paris). *Compt. Rend.*, 1959, **248** (4), 504–507.—After collection of the sample (dust filtered from air, or vapours aspirated through dil. NaOH soln.), the $F^-$ are separated from interfering ions ($PO_4^{3-}$, $SO_4^{2-}$) by distillation in superheated steam in the presence of $H_2SO_4$ and of $SiO_2$ (Fabre *et al.*, *Ibid.*, 1955, **240**, 226). From 1 to 100 μg of $F^-$ in the neutralised distillate can then be determined by titration with 0·004 *M* $Th(NO_3)_4$ in a white porcelain dish until the colour of the indicator {1 ml of 0·02% soln. of

SPADNS [sodium 1:8-dihydroxy-2-(4-sulphophenylazo)naphthalene-3:6-disulphonate] plus 1 ml of pH 3·1 buffer} changes from red to violet. The accuracy is within 3%, and the sensitivity is claimed to be adequate for the control of industrial hygiene. The procedure is applicable to biological samples ($H_2O$, alcoholic drinks, bone, blood and urine) provided that $F^-$ are fixed by ignition at $\simeq 500°$ with a mixture of MgO and Mg acetate and are then liberated by distillation.

W. J. BAKER

4759. **New spot test for the detection of fluoride ion.** R. Belcher, M. A. Leonard and T. S. West (Chem. Dept., Univ., Edgbaston, Birmingham, England). *Talanta*, 1959, **2** (1), 92–93.—Fluoride ions change the red colour of the $Ce^{III}$ chelate of alizarin complexone (1:2-dihydroxyanthraquinon-3-ylmethylamine-NN-diacetic acid (**I**) to lilac blue. *Procedure*—Mix one drop of the test soln. with one drop of a 0·001 *M* soln. of **I** buffered to pH 4·3 with Na acetate - acetic acid. Add, with stirring, one drop of 0·001 *M* $Ce(NO_3)_3$. The limit of identification is 0·2 $\mu$g and the dilution limit 1 in $1·8 \times 10^6$. Serious interference is caused by phosphate, strong organic chelating agents and certain heavy metals.

W. T. CARTER

4760. **Amperometric determination of fluoride at a rotated aluminium electrode.** I. M. Kolthoff and C. J. Sambucetti (Sch. of Chem., Univ. of Minnesota, Minneapolis, U.S.A.). *J. Amer. Chem. Soc.*, 1959, **81**, 1516–1517.—A rotated aluminium electrode ($\frac{1}{16}$ in. diam., 0·15 sq. cm surface area, 600 r.p.m.) is readily polarised in $HNO_3$ soln. of pH $\gg$ 2, and in a soln. buffered with acetate at pH 3 to 5·5. In the absence of O, the limiting currents at $-$ 0·75 V are proportional to the $F^-$ concn. from $10^{-5}$ *M* to $3 \times 10^{-4}$ *M*. Amperometric titrations with $Al(NO_3)_3$ soln. in an acetate basal soln. at pH 3·5 give good results. It is claimed that the electrode acts as a pF electrode in acid soln. The results of Baker and Morrison (*cf. Anal. Abstr.*, 1955, **2**, 3350) could not be reproduced.

T. R. ANDREW

4761. **Determination of small amounts of fluorine in foods and water. II. Qualitative detection of fluoride.** K.-E. Quentin, J. Indinger and S. W. Souci (Balneologische Inst., Univ. Munich, Germany). *Z. LebensmittUntersuch.*, 1959, **109** (3), 213–218.—Fluorine is isolated as HF from aq. soln. (concentrated by evaporation if necessary) by micro-distillation into a suspended drop of water in the Feigl apparatus, which consists of a weighing bottle, the stopper of which has a projection on the underside for the suspension of the drop of water. The test soln. (a few ml) is gently heated with a few drops of $H_2SO_4$ and a little tartaric acid to the point of incipient browning, after which the drop of water (containing 25 to 33% of the available HF) is transferred to a spot-testing tile, and tested in comparison with standard soln. of NaF (5 to 250 $\mu$g per litre) by the addition of 50% acetic acid and zirconium - haematoxylin indicator (one drop of each). As little as 0·2 $\mu$g of F can be detected by the colour change. For a semi-quant. determination, a factor of 3·5 is applied to compensate for the incomplete recovery of the available HF from the test soln.

P. S. ARUP

4762. **Determination of small amounts of fluorine in alumina-containing materials.** E. Abrahamczik and W. Merz (Badischen Anilin- & Soda-Fabrik A.-G., Ludwigshafen/Rhein, Germany). *Mikrochim. Acta*, 1959, (3), 445–455.—Fluorine in ores and catalysts containing $Al_2O_3$ as carrier material may be rapidly determined down to 5 p.p.m. with a relative accuracy, depending on the $F^-$ content, of between 2 and 5%. The separation of $F^-$ (as HF) is cleanly and selectively accomplished from most other interfering elements by fusing the specimen (1 g) with $K_2S_2O_7$ in a quartz flask having a side-arm which projects into the melt and through which a strong air-blast is led to drive off the HF, which is absorbed in *N* NaOH. Quantitative removal of the remaining traces of interfering ions is carried out by steam-distillation from $HClO_4$ into 0·1 *N* NaOH. The determination is finished by titration with $Th(NO_3)_4$ soln., with a mixed indicator of Na alizarinsulphonate and methylene blue.

D. F. PHILLIPS

4763. **Argentimetric determination of chloride by Volhard's method and a study of various modifications.** O. Alcides Ohlweiler, J. de Oliveira Meditsch and S. Kuperstein (Escola de Engenharia, Porto Alegre, R.G.S., Brazil). *Chim. Anal.*, 1959, **41** (3), 94–96.—Suggested modifications to Volhard's method to eliminate error due to reaction between AgCl and $SCN^-$ (filtration of AgCl, addition of nitrobenzene, or of large amounts of $Fe^{3+}$) are critically examined. Three procedures are recommended, the first being the most accurate. (*i*)—Weigh 10 g of 0·4 *N* NaCl (from a weight burette) into a beaker, add $H_2O$ (10 ml) and 6 *N* $HNO_3$ (5 ml) and a weighed excess of 0·1 *N* $AgNO_3$ (2 to 5 g excess). Stir for 5 min. then filter and wash the ppt. with $HNO_3$ (1:99) (10 × 10 ml). To the filtrate and washings add 40% $(NH_4)_2SO_4.Fe_2(SO_4)_3$ soln. (1 ml) and a weighed amount of 0·1 *N* KSCN, then complete the titration with 0·01 *N* KSCN to a red colour stable for 1 min. (*ii*)—To 10 g of 0·4 *N* NaCl add $H_2O$, $HNO_3$ and $AgNO_3$ soln. as before. Add nitrobenzene (3 ml), then $(NH_4)_2SO_4.Fe_2(SO_4)_3$ soln. and 0·1 *N* KSCN, and complete the titration as before. (*iii*)—To 10 g of 0·4 *N* NaCl add $H_2O$ (10 ml) and 6 *N* $HNO_3$ (17 ml), then 2 *M* $Fe(NO_3)_3$ (10 ml) and 1·00 ml of 0·01 *N* KSCN. Add a weighed amount of 0·1 *N* $AgNO_3$ and complete the titration with 0·01 *N* $AgNO_3$ to the discharge of the red colour. Standard deviations for the 3 methods are $\pm$0·00024, $\pm$0·00041 and $\pm$0·00030 g, respectively (each based on 5 determinations).

P. D. PARR-RICHARD

4764. **Precision null-point potentiometry. A simple, rapid and accurate method for determination of low concentrations of chloride.** H. V. Malmstadt and J. D. Winefordner (Univ., Urbana, Ill., U.S.A.). *Anal. Chim. Acta*, 1959, **20** (3), 283–291.—With the apparatus and procedure described, concn. of $Cl^-$ from $10^{-6}$ to $10^{-1}$ *M* can be determined in a few minutes with an error of $\simeq$ 0·1%. The concn. of $Cl^-$ in the sample is changed, while keeping the ionic strength constant, until it is identical with that of the standard reference soln., *i.e.*, zero potential is attained across the two silver - silver chloride electrodes, one in each soln. If the concn. of $Cl^-$ in the sample soln. is higher than that in the reference soln., dilution to the null point is effected by the addition of *M* $H_2SO_4$, but if it is lower a soln. twice as conc. in $Cl^-$ as the reference soln. is added. The ionic strength of all soln. is kept constant by the addition of *M* $H_2SO_4$ and diluting to the correct vol. The only calculation needed is either a simple addition or subtraction; the control of temp. and corrections for

$Cl^-$ in the reagents, etc., are obviated. The method is specially applicable when the concn. of $Cl^-$ in a series of samples varies over a relatively small range. There is a slow drift of electrode potential when $Br^-$ are present. W. J. BAKER

4765. **Rapid determination of chloride in silica or other solids.** J. W. Robinson (Esso Standard Oil Co., Baton Rouge, La., U.S.A.). *Anal. Chim. Acta*, 1959, **20** (3), 256–258.—The sample (> 1·5 g) is heated to fuming in a porcelain boat with a mixture (9:1) of conc. $H_2SO_4$ and conc. $HNO_3$ in a furnace (max. ≃ 590° F) in a stream of N. The evolved $Cl^-$ are collected in 100 ml of 2% $Na_2CO_3$ soln. and determined either colorimetrically with $Hg(SCN)_2$ and $(NH_4)_2SO_4.Fe_2(SO_4)_3$, or by potentiometric titration in acetone soln. with $AgNO_3$ soln. at pH 2. An analysis takes ≃ 20 min. and the accuracy is satisfactory. W. J. BAKER

4766. **Determination of chlorides in zinc electrolytes by non-compensated potentiometric titration.** Z. I. Ivanova and P. N. Kovalenko (Rostov State Univ.). *Zavod. Lab.*, 1959, **25** (3), 290–291.—With a mercury indicator electrode and a tungsten reference electrode the soln. is titrated with 0·1 *N* $Hg(NO_3)_2$. G. S. SMITH

4767. **Simultaneous determination of chlorite and hydrogen peroxide in the presence of chlorides, chlorates, carbonates and caustic alkalis [in production control of sodium chlorite].** A. I. Kachalov and I. G. Bŷkova. *Zavod. Lab.*, 1959, **25** (3), 289–290.—The sample (10 ml) is boiled with 100 ml of water and 0·2 to 0·4 g of $PbO_2$ for 10 to 15 min., the cooled soln. is treated with 20 ml of 10% KI soln. and 10 ml of dil. $H_2SO_4$ (1:1), and the iodine liberated is titrated with 0·1 *N* $Na_2S_2O_3$ to give the $NaClO_2$ content. The total of $H_2O_2$ and $NaClO_2$ is determined on another portion without the use of $PbO_2$, and $H_2O_2$ is obtained by difference. G. S. SMITH

4768. **Coulometric titrations of mixtures of perchloric acid and acetic acid in water - acetone medium.** R. Rosset and B. Trémillon (Lab. de Chim. Anal., École Sup. de Phys. et de Chim. Ind., 10, rue Vauquelin, Paris, France). *Bull. Soc. Chim. France*, 1959, **26** (1), 139–144.—In acetone - water soln. (4:1), $HClO_4$ and acetic acid are neutralised independently at different potentials. An arrangement is described in which the soln. is electrolysed at constant current, with $NaClO_4$ as basal electrolyte, with a platinum cathode providing the $OH^-$ and a silver - silver chloride electrode dipping into NaCl soln. separated from the cathode compartment by a sintered glass disc. The indication of the two end-points is effected by plotting the current in an indicator electrode circuit with ≃ 100 mV constant p.d. or with 10 to 15 mV constant p.d. Alternatively, the voltage of the indicator electrodes for a constant current is measured. In this way mixtures ≃ 0·001 *M* with respect to each acid are determined to within ≃ 1%. The theory of the coulometric neutralisation and of the function of the indicator electrodes is discussed. E. J. H. BIRCH

4769. **Titration of periodates in the presence of iodate with hydrazine sulphate.** A. Berka and J. Zýka (Dept. Anal. Chem., Charles' Univ., Prague). *Českosl. Farm.*, 1959, **8** (3), 136–138.—In soln. buffered with $NaHCO_3$, borate or Na acetate (pH 7·5 to 9), periodate can be titrated potentiometrically with a soln. of hydrazine sulphate according to the equation—

$$2IO_4^- + N_2H_4 = 2IO_3^- + N_2 + 2H_2O.$$

The determination of 10 to 20 mg of $KIO_4$ can be carried out in the presence of a 20-fold excess of iodate. The procedure is reliable for the titration of the excess of periodate in the indirect determination of organic compounds. J. ZÝKA

4770. **Titrimetric determination of manganese following nitric acid oxidation in the presence of pyrophosphate.** C. O. Ingamells (Rock Anal. Lab., Univ. of Minnesota, Minneapolis, U.S.A.). *Talanta*, 1959, **2** (2), 171–175.—Bivalent Mn is oxidised to $Mn^{III}$ and titrated with ferrous soln., with diphenylamine as indicator. To the Mn soln., preferably containing $HNO_3$ as the only acid, add 10 ml of 85% $H_3PO_4$ plus an additional 15 ml for each 40 mg of MnO expected. Add 5 ml of $HNO_3$ and evaporate on a hot-plate, without boiling, till the vol. is reduced to that of the $H_3PO_4$ added. Then add 5 to 6 g of $Na_4P_2O_7$ for each 20 ml of $H_3PO_4$ and heat till the $HNO_3$ is expelled, as shown by absence of condensation on the walls of the flask. Add 1 ml of $HNO_3$ (1:1, boiled to remove oxides of N) and heat for 10 to 15 min., but without removal of all $HNO_3$. Cool until the flask can be handled, then add one-quarter of the vol. of cold water, mix, and cool in running water. Dilute with water to about 20% in $H_3PO_4$, cool in running water, and titrate with 0·1 or 0·02 *N* $(NH_4)_2SO_4.FeSO_4$ soln. in 5% $H_2SO_4$ (freshly prepared with boiled water), adding the indicator (1% soln. of diphenylamine in conc. $H_2SO_4$, or 0·2% aq. Ba diphenylaminesulphonate soln.) just before the end-point, when the pink colour of $Mn^{III}$ is almost discharged. The end-point is very sharp. With > 40 mg of MnO in 15 ml of $H_3PO_4$ oxidation may be incomplete, a safe limit being 2 mg of MnO per ml. Results for garnet, phosphate minerals, bauxite, Ni - Cr steel, and Fe and Mn ores agree well with those by gravimetric and colorimetric procedures. Modifications required for the preliminary dissolution of some of these materials are discussed. R. E. ESSERY

4771. **Micro-determination of iron by means of catalysis.** L. Erdey and F. Szabadváry (Inst. f. allg. Chem. der Tech. Univ. Budapest, Hungary). *Mikrochim. Acta*, 1959, (3), 424–431.—The reaction between $H_2O_2$ and Variamine blue is catalysed by $Fe^{III}$, and this effect can be utilised for the determination of Fe. The method is based on measurement of the time required for the photometer galvanometer to reach a pre-determined scale division for a sample to which no Fe has been added. This measurement is then repeated in the presence of a known amount of Fe. Finally the reaction time is measured on the sample on which Fe is to be determined. The unknown amount of Fe may be calculated from the three reaction times. By this means it is possible to determine as little as $2 \times 10^{-5}$ g of Fe per ml. D. F. PHILLIPS

4772. **Analytical applications of the complexones. XVI. Indicators for the macro- and micro-volumetric determination of iron with 1:2-diaminocyclohexane-NNN′N′-tetra-acetic acid.** F. Bermejo Martínez and R. Rey Mendoza (Lab. de Quím. Anal., Fac. de Ciencias, Santiago de Compostela, Spain). *Quím. e Ind., Bilbao*, 1959, **6** (1), 3–7.—Sulphosalicylic acid (**I**), tiron (**II**) and KSCN were used as indicators for the volumetric determination of

$Fe^{3+}$ with 1:2-diamino*cyclo*hexane-NNN′N′-tetra-acetic acid. The best results were given by **I** (3 ml of 2% soln.) at 50° and pH 2 to 5, but they were 1 to 3% high; the best results for **II** (2 ml of 2% soln.) at 50° and pH 2 to 4 were 1 to 4% high. Better results were obtained when KSCN (2 *M*) was used, although the amount of indicator had some effect on the results. For soln. containing 30 to 120 mg of Fe, and 15 ml of KSCN soln., the results were up to 0·5% high. It was found necessary to use 10 ml of amyl alcohol or diethyl ether to obtain a sharp end-point in the micro-titration of soln. containing up to 12 mg of Fe, and results were then within ± 0·5% of the theoretical. G. H. FOXLEY

4773. **Photometric titration of iron with ethylene-diaminedi-(o-hydroxyphenylacetic acid).** A. L. Underwood (Emory Univ., Atlanta, Ga., U.S.A.). *Anal. Chim. Acta*, 1959, **20** (3), 228–232.—Less than 1 mg of $Fe^{3+}$ in 100 ml of soln. can be titrated at pH 3·5 with a 0·01 *M* soln. of ethylenediamine-di-(*o*-hydroxyphenylacetic acid), the end-point being found photometrically at 470 mμ. The error is < 1%; Th, Ag, Cu and Al interfere, but not Mg, Ca, $Cr^{III}$, $Mn^{II}$, $Co^{II}$, Zn, Cd, $Hg^{II}$, Pb and Ni. Microgram amounts of Fe can be determined by scaling down the vol. of soln. and the titrant concn., and milligram amounts by changing to a wavelength (550 mμ) at which the sensitivity is less. W. J. BAKER

4774. **Spectrophotometric determination of iron with 3-hydroxy-3-methyl-1-phenyltriazen.** H. K. L. Gupta and N. C. Sogani (Chem. Dept., Gov. Coll., Ajmer). *J. Indian Chem. Soc.*, 1959, **36** (2), 87–91.—Ferric iron forms a greenish blue, water-soluble complex with 3-hydroxy-3-methyl-1-phenyl-triazen $[C_6H_5N{:}N{\cdot}N(CH_3)OH]$ in the pH range 3·1 to 4·5, with an absorption peak at 625 mμ. The reaction is used for the direct spectrophotometric determination of Fe in the presence of almost all the commonly associated elements. The system obeys Beer's law in the concn. range 1 to 10 p.p.m. of Fe. The sensitivity of the colour reaction determined in Nessler cylinders is 1 part of Fe in $4{\cdot}5 \times 10^6$ parts of soln. and on a spot plate is 0·1 μg of Fe. The complex has the formula $FeR_2$ (R = reagent). The molecular extinction coefficient at 625 mμ and the dissociation constant at 34° are $2{\cdot}8 \times 10^3$ and $1{\cdot}156 \times 10^{-11}$, respectively. I. JONES

4775. **Determination of bivalent and tervalent iron with a dithiocarbamoylhydrazinium salt by colorimetric or spectrophotometric means.** A. Musil and W. Haas (Inst. f. anorg. u. anal. Chem., Univ., Graz, Austria). *Mikrochim. Acta*, 1959, (3), 481–487.—Bivalent Fe reacts with a dithiocarbamoyl-hydrazinium salt to form a violet complex in acetate buffer soln., which has an absorption max. at 570 mμ. This reaction may be used for the determination of $Fe^{2+}$ in the concn. range 0·01 to 5 μg per ml. After reduction with ascorbic acid, $Fe^{3+}$ may also be determined by this method. The interfering effects of other cations and their max. permissible concn. have been determined. D. F. PHILLIPS

4776. **Rapid method of determining iron in cement.** N. S. Frumina (N. G. Chernȳshevskiĭ Saratov State Univ.). *Zavod. Lab.*, 1959, **25** (2), 148–149.—The sample (0·25 g) is dissolved by boiling with 10 ml of conc. HCl containing 0·5 g of $NH_4Cl$, and the soln., without being filtered, is titrated hot with 0·5 *N* $SnCl_2$ until the colour is light yellow. Indigo carmine soln. (25%) (3 to 4 drops) is added and the titration is continued slowly until the colour changes from green to blue and then to colourless. Addition of 0·05 *N* $K_2Cr_2O_7$ (possibly 3 or 4 drops) is now made until a stable blue colour appears. (If one drop is sufficient just the right amount of $SnCl_2$ soln. has been used.) The excess of $K_2Cr_2O_7$ is determined by titration with a soln. of $Fe^{2+}$ in the presence of 3 to 4 drops of 0·1% phenylanthranilic acid as indicator. The method takes 10 to 12 min. G. S. SMITH

4777. **Gases in ferro-alloys.** N. Christensen (SINTEF, Tech. Univ. of Norway, Trondheim). *Tidsskr. Kjemi Bergv.*, 1959, **19** (3), 57–61.—The chemical bonding of O, N and H in different ferro-alloys is discussed. Typical analytical data on the contents of O, N and H in some commercial alloys are presented. The estimated amount of gaseous impurities introduced into steel baths by ferro-alloy additions is given. The sampling of ferro-silicon and the determination of H in that alloy is discussed (Christensen and Gjermundsen, *J. Iron St. Inst.*, 1958, **190**, 248). B. RÖNNHOLM

4778. **Apparatus for carbon content [of steel] determination.** R. Rew (B.C.I.R.A. Res. Dept., Bordesley Hall, Alvechurch, Birmingham). *J. Res. Brit. Cast Iron Ass.*, 1959, **7**, 651–655.—An improved layout, furnaces and oxygen control for the determination of C in iron and steel are described. C. H. COWPER-COLES

4779. **Determination of major constituents in alloy steels by spectrographic solution methods.** C. A. Waggoner (Pacific Naval Lab., Esquimalt, B.C., Canada). *Appl. Spectroscopy*, 1959, **13** (2), 31–33.—Stainless steels can be analysed spectrographically by adapting either the porous cup or rotating disc soln. techniques. The procedure described is most useful if no standard alloys are available and if the samples vary in size and shape. Cobalt is used as an internal standard and Fe, Cr, Ni, Mn and Mo can be determined to within ± 3% of the amounts present. Inter-element effects arising from wide variations in composition are negligible. The method could probably be extended to low-alloy steels and nickel-base alloys containing Fe and Cr. K. A. PROCTOR

4780. **Alkalimetric determination of phosphorus [in steel] as quinoline molybdophosphate.** G. Alfelt (Air Force Central Lab., Malmslätt, Sweden). *Jernkontor. Ann.*, 1959, **143** (3), 167–174.—The pptn. of quinoline molybdophosphate (**I**) in various media was studied. In 0·5 *M* to 5 *M* $HNO_3$ the pptn. of **I** is quant. The presence of $Fe^{3+}$ as nitrate alters the highest permissible acid concn. to 4 *M* $HNO_3$ and as chloride to 3 *M* $HNO_3$. Tartaric acid (< 0·4 g) has no influence on the pptn. In 0·5 *M* to 1·75 *M* HCl the pptn. of **I** is quant. In the presence of $Fe^{3+}$ the highest permissible acid concn. is 1 *M* HCl. In 1 *M* to 4 *M* $HClO_4$ the pptn. of **I** is quant. Generally the amount of reagent required for the quant. pptn. of **I** is increased in more acid soln. *Reagent*—Dissolve $Na_2MoO_4.2H_2O$ (100 g) in $H_2O$ (250 ml), add HCl (sp. gr. 1·19, 115 ml) and $HNO_3$ (sp. gr. 1·40, 100 ml). Add this soln. to a soln. of quinoline (14 ml) in a mixture of $H_2O$ (160 ml), conc. HCl (75 ml) and conc. $HNO_3$ (60 ml). Add $H_2O$ (500 ml) and filter after 24 hr. Store in a polyethylene vessel. *Procedure for steel soluble in $HNO_3$*—Dissolve the sample (2 g) in $HNO_3$ (1:1) (40 ml), heat to

boiling, add $KMnO_4$ soln. (3%, w/v) (5 ml), boil, add tartaric acid soln. (20%, w/v) (2 ml), boil, add $H_2O$ (80 ml), heat to boiling and add reagent (25 ml). Filter, wash the ppt. with 1 *M* $HNO_3$ and 0·2 *M* $KNO_3$, then dissolve it in $H_2O$ and standard NaOH soln. Back-titrate with standard HCl soln. against a mixture (2:3) of phenolphthalein and thymol blue (both 0·1% in ethanol). Procedures are also given for steel insoluble in $HNO_3$. The reported results show good precision and accuracy. B. RÖNNHOLM

4781. **Colorimetric determination of traces of selenium in steel. I. Determination of small quantities of selenium in the absence of other elements.** N. Leontovitch (Inst. Rech. de la Sidérurgie, Saint-Germain-en-Laye, France). *Chim. Anal.*, 1959, **41** (2), 56–62.—In the preliminary investigation described, the effect of reagents and conditions on the production of suspensions of Se by reduction was studied. Reduction with hydrazine hydrochloride in the presence of formic acid has certain advantages, *viz*, in moderate concn. formic acid is a good solvent for tellurium dioxide, it does not absorb significantly below 270 mμ, neither tellurous nor telluric acid (in amounts of 1 mg of Te per 50 ml) increases the extinction of 6 *N* formic acid, and oxygenated compounds of Te are not reduced under the conditions used. *Procedure*—The test soln. (10 ml) (containing ⩾ 500 μg of Se in the form of an oxygenated compound) is placed in a 25-ml flask and the following reagents are added successively, with shaking after each addition—10 ml of 15 *N* formic acid, 2·5 ml of poly(vinyl alcohol) soln. (20 mg per ml), 1 ml of 10% hydrazine hydrochloride soln. and water to 25 ml. A reference soln. is made from the same reagents and subjected to the same treatment. After being heated at 93° to 95° in a boiling-water bath for 5 min. the soln. is cooled and the extinction is measured at 315 mμ in a 1-cm cell and compared with that of the blank. Standards should be prepared for each series of determinations and used to give absolute values. The method is sensitive to 2 μg of Se per ml. S. M. MARSH

4782. **Determination of the tungsten content in alloyed steels by the β,γ-reflection method.** J. Fodor (Csepel Iron and Metal Works, Budapest). *Acta Chim. Acad. Sci. Hung.*, 1959, **19** (4), 327–335 (in English).—By measurement of the radiation from a surface irradiated by a β-source, W in steel can be determined within 1% absolute. The source is a film of $^{204}Tl$ deposited on the inner surface, inclined at an angle of 45°, of a copper ring. The radiation returning through the ring consists of reflected β- and secondary γ-radiation, which is measured with a scintillation counter. One type of radiation characteristic of W is selected by a discriminator. The radiation to be selected is established with the aid of a tungsten plate. The calibration curve is rectilinear from 1% to 18% of W. Sampling takes 2 min. and the measurement takes 100 sec. The activation method used to check the calibration samples is described. G. BURGER

4783. **Sodium *p*-(mercaptoacetamido)benzenesulphonate as colorimetric reagent for cobalt.** H. K. L. Gupta and N. C. Sogani (Gov. College, Ajmer, India). *Anal. Chem.*, 1959, **31** (5), 918–920.—Sodium *p*-(mercaptoacetamido)benzenesulphonate (**I**) forms water-sol. brownish-red complexes (Co - $\mathbf{I}_3$) with $Co^{II}$. Between pH 6·5 and 7·5 the absorption max. is at 475 mμ, and between pH 8·5 and 11·0 at 390 mμ. Both max. are suitable for colorimetry but that at 475 mμ is preferable; $Ni^{II}$ and Fe also form complexes, and interference by Ni cannot be completely excluded except by separating the metals. Beer's law holds in the range 0·3 to 2 p.p.m. of Co (reproducibility not given). The method is suitable for the determination of 15 to 100 μg of Co in the presence of Zn (200), Mn (200), Cu (150), Fe (150), Al (300), Cr (150), Ag (150), Pd (5), $WO_4^-$ (150) and $MoO_4^-$ (150 p.p.m.). *Procedure*—To the Co soln. (15 to 100 μg of Co) add 10% Na K tartrate soln. (2 ml), buffer (pH 7·0) (5 ml) and 1% **I** soln. (5 ml). Place in a boiling-water bath for 5 to 7 min., make up to 50 ml, and read the extinction at 475 mμ against $H_2O$. In the presence of Fe, adjust the pH to between 2 and 4 with HCl before dilution. J. P. STERN

4784. **Determination of trace amounts of cobalt in iron and steel and some associated materials.** BISRA Methods of Analysis Committee. *J. Iron St. Inst.*, 1959, **191** (3), 236–240.—The recommended method is satisfactory for determining < 0·04% of Co in iron and steel, ferro-alloys of Mn, Ti, Ni and Cr, chromium and nickel metals and iron ore. Reproducibilities of ±0·001% for ⩾ 0·01% of Co and ±0·002% for ⩾ 0·04% of Co are claimed. The method involves photometric measurement of the cobalt complex with nitroso-R salt after separation by ZnO and pptn. of Co with 1-nitroso-2-naphthol. J. W. O. PYEMONT

4785. **New colour reaction for the identification of the nickel ion.** S. Popa and G. Furnică. *Acad. R.P.R., Stud. Cercet. Chim.*, 1959, **6** (3), 481–488.—The study of the microcrystalline structure of the sodium, ammonium and nickel salts of ethylphosphono- and diethylphosphino-dithioic acids enables these two acids to be separated and identified. The nickel salt of the former acid gives a characteristic violet-coloured ether extract; $Zn^{2+}$, $Mn^{2+}$, $Hg^{2+}$, $Ba^{2+}$, $Mg^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $Ca^{2+}$, $Bi^{3+}$, $Al^{3+}$, $Sn^{2+}$, $Ag^+$, $Pb^{2+}$ and $K^+$ do not interfere. The yellow-green colour given by the ether extract of the $Co^{2+}$ salt masks that of $Ni^{2+}$ only if the Co is in large excess, but this in turn can be suppressed by a large excess of the organic reagent. The sensitivity of the reagent is only slightly less than that of dimethylglyoxime (≃ 1·31 μg), but it is more specific. H. SHER

4786. **Spectrophotometric determination of traces of nickel with 4-*iso*propylcyclohexane-1:2-dione dioxime.** B. L. McDowell, A. S. Meyer, jun., R. E. Feathers, jun., and J. C. White (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 931–934.—The high extraction coeff. of the complex of $Ni^{2+}$ with 4-*iso*propylcyclohexane-1:2-dione dioxime (**I**) in xylene permits the extraction of 10 μg of Ni from 500 ml of aq. soln. and its spectrophotometric determination with an accuracy within ± 2%. Co-extracted Cu (⩾ 800 μg) can be removed from the xylene phase by a single wash with 5% thioacetamide soln. (5 ml). Interference by Fe (200-fold excess) can be masked by $F^-$ (0·6 g). *Procedure*—Adjust the pH of the aq. soln. of Ni (10 to 150 μg) to approx. 7 and add sufficient 10 *M* ammonium acetate to make the final soln. 1 *M* with respect to acetate. Add 2 ml of 0·004 *M* aq. **I** per 100 ml of soln. After 30 min. extract with xylene (10 ml) and measure the extinction of the xylene soln. at 383 mμ. J. P. STERN

4787. **Spectrophotometric determination of nickel with mercaptoacetic acid.** P. C. Christopher and H. W. Hamme (Chemstrand Corp., Pensacola, Fla., U.S.A.). *Appl. Spectroscopy*, 1959, **13** (1), 7–10.—The method is sensitive to 0·001 mg of Ni per ml and Beer's law is followed up to concn. of 0·7 mg per ml. The optimum working range, within which the error is 3%, is 0·04 to 0·5 mg of Ni per ml. The colour produced is stable for several hours and is unaffected by changes in pH as long as the soln. is alkaline. A preliminary separation of the Ni by dimethylglyoxime extraction eliminates interfering metals, and the addition of Na citrate before development of the colour prevents interference from metals extracted with the Ni. K. A. PROCTOR

4788. **Precipitation of nickel(II) sulphide from acid solutions by thioacetamide.** D. F. Bowersox, D. M. Smith and E. H. Swift (California Inst. of Technol., Pasadena, U.S.A.). *Talanta*, 1959, **2** (2), 142–153.—An equation is given for calculating the rate of pptn. of $Ni^{2+}$ as sulphide by thioacetamide (**I**) from acid soln. at 90° ± 1°, and the conditions for the separation of Pb and Cd from Ni at 90° and pH 1 to 2 are discussed. Hydrogen ion concn. and time are critical factors in the separation of Pb, Cd and other $H_2S$-group metals from Ni by pptn. with $H_2S$ from soln. of **I**. The equation permits the calculation of the amount of Ni which would be co-pptd. by direct reaction with **I** under given conditions, and it appears that the pptn. of Pb, Cd, etc., with sulphide from soln. of **I** should be carried out at the lowest permissible pH and in the shortest permissible time to obtain effective separation, and that the ppt. should be removed from the soln. as soon as quant. separation has been achieved. Precipitation conforming to the equation is obtained at $H^+$ concn. at which pptn. by $H_2S$ does not occur, and the rate of formation of NiS is independent of the quantity of metal sulphide present, and of the concn. of $Pb^{2+}$, $Cd^{2+}$ and $H_2S$ in the soln. It is pointed out that complex ion effects may seriously affect equilibrium and rate conditions, and that caution is needed when substituting **I** for $H_2S$ in analytical separations.
R. E. ESSERY

4789. **Determination of nickel in gold - nickel alloys.** D. H. Wilkins and L. E. Hibbs (Gen. Electric Co., Schenectady, N.Y., U.S.A.). *Anal. Chim. Acta*, 1959, **20** (3), 273–274.—The Ni is separated by passing the sample soln. (adjusted to 2 *N* in HCl) through a long column of strongly basic anion-exchange resin, whereby the Au complex is firmly retained at the top of the column. The Ni is eluted with 2 *N* HCl, and can then be determined by the back-titration of an excess of 0·03 *M* EDTA with 0·03 *M* CuSO, with 1-(2-pyridylazo)-2-naphthol as indicator. The error is ≃ + 0·2%. Successive samples can be analysed until the Au complex is near the base of the column.
W. J. BAKER

4790. **Spectrophotometric determination of ruthenium with 1-naphthylamine-3:5:7-trisulphonic acid.** E. L. Steele and J. H. Yoe (Dept. of Chem., Univ., Charlottesville, Va., U.S.A.). *Anal. Chim. Acta*, 1959, **20** (3), 211–215.—From 0·5 to 14 p.p.m. of Ru can be determined by measuring the extinction at 530 mμ of the stable red complex formed at pH 2·5 to 5 (dil. HCl) between 1-naphthylamine-3:5:7-trisulphonic acid ($5 \times 10^{-4}$ *M* aq. soln.) and $Ru^{VI}$. The reaction is rapid at 15° and the complex, which obeys Beer's law, has the formula $(\text{reagent})_2RuO_4$. All interfering ions should be removed by first boiling off Os as the tetroxide from conc. $HNO_3$ soln., followed (after addition of $KMnO_4$) by a second distillation to collect $RuO_4$ in the reagent (5 or 25 ml). The sensitivity is 0·1 μg per ml. W. J. BAKER

4791. **Gravimetric determination of palladium with 2-*o*-hydroxyphenylbenzoxazole.** R. F. Wilson and L. J. Baye (Dept. of Chem., Texas Southern Univ., Houston, U.S.A.). *Z. anal. Chem.*, 1959, **166** (5), 359–361 (in English).—*Procedure*—Palladium is treated with hot fuming $HNO_3$. To 1 vol. of soln. containing 2 to 30 mg of Pd are added, with stirring, 2 vol. of ethanol and 1 vol. of a satd. ethanolic soln. of 2-*o*-hydroxyphenylbenzoxazole. The ppt. is filtered off immediately on a medium-porosity sintered glass crucible, washed several times with 50% ethanol, and dried at 110° for 1 hr. Cations that interfere are listed.
B. B. BAUMINGER

4792. **Spectrophotometric determination of palladium with phenyl 2-pyridyl ketoxime.** Buddhadev Sen (Coates Chem. Lab., Louisiana State Univ., Baton Rouge). *Anal. Chem.*, 1959, **31** (5), 881–884.—The $Pd^{II}$ chelate of phenyl 2-pyridyl ketoxime (**I**) contains 2 moles of **I** per mole of Pd and has absorption max. at 340 and 410 mμ (ε 50,000 and 30,000, respectively) in $CHCl_3$, which can be used for the determination in 1-cm cells of 1·5 to 8 and 2 to 10 p.p.m. of Pd, respectively. The colour of the chelate is stable; 5 mg of Be, Mg, Sr, Ba, Zn, Cd, $Hg^{II}$, Al, Pb, $Bi^{III}$, $VO^{2+}$ $Mn^{II}$, $Fe^{III}$, $Ru^{VI}$, $Rh^{III}$, $Os^{VI}$, Ir, Pt and Ag do not interfere with the determination of Pd (100 μg). Interference by $Cu^{II}$, $Fe^{II}$, $Co^{II}$ and $Ni^{II}$ is eliminated with EDTA. Only $Au^{III}$ and $CN^-$ interfere seriously. *Procedure*—To the Pd soln. add a 1% ethanolic soln. of **I** (2 ml), dilute to 15 ml, adjust to pH 8·5 to 10 with aq. $Na_2CO_3$ soln. and extract twice with 10 ml of $CHCl_3$. Separate the organic phase and make it up to 25 ml. Measure the extinction. J. P. STERN

4793. **Application of organoselenium compounds in analytical chemistry. II. The determination of palladium and other metals with N-acetyl-N′-phenylselenourea.** F. Pino Pérez, F. Burriel-Martí and L. Martínez Conejero (Dept. de Quím. Anal. del C.S. de I.C. Madrid y La Laguna, Spain). *Inf. Quím. Anal.*, 1959, **13** (2), 38–51.—*Qualitative tests*—One drop of an alcoholic soln. of N-acetyl-N′-phenylselenourea (0·1 g per 100 ml) is added to two drops of a soln. of a metal (0·1 g per 100 ml). Precipitates or turbidities are formed by Os, Pd, Pt, Au, Hg and Ag, and the effects of dil. $HNO_3$ (1:1), aq. $NH_3$ (10%) and KCN soln. (10%) on the ppt. are noted. The sensitivity is 1 μg for Pd (dilution limit $6·7 \times 10^{-6}$). *Quantitative use*—Bivalent Pd forms a complex with N-acetyl-N′-phenylselenourea, which is stable at pH values < 3 and > 8·4, and which has max. extinction at 470 mμ; $Cu^{2+}$ interfere. The determination of $Ag^+$ is similar to that for $Pd^{2+}$, but the determination of $Pt^{4+}$ is unsatisfactory. The selectivity of the reagent is attributed to the –CSe·NH– group.
G. H. FOXLEY

4794. **5-Aminothiazoline-2-thiocarboxyamide used as analytical reagent. II. The palladous compounds, their composition and analytical applications—heterometric titration.** Ping-Shih T'ien and K'uei Wang (Dept. of Chem., Peking Med.

Coll.). *Acta Chim. Sinica*, 1959, **25** (2), 85–91.—5-Aminothiazoline-2-thiocarboxyamide (**I**) (*cf. Anal. Abstr.*, 1958, **5**, 4145) is used in the determination of micro quantities of Pd by heterometric titration in 95% ethanol with an error $\Rightarrow \pm 3{\cdot}5\%$. EDTA is added to obviate interference by foreign metals, *e.g.*, Ca, Ba, Zn, Mn, Co, Fe, Cr, Pb, Pt, Cu, Ce and Cd. In weakly alkaline aq. and alcoholic soln., two palladous compounds with the ratios of **I** to Pd of 1:1 and 2:1 have been identified. S. H. YUEN

4795. **Rapid and precise micro-heterometric determination of gold, palladium or platinum with nitron in thiocyanate solutions. A study of the reactions and compounds.** M. Bobtelsky and J. Eisenstadter (Hebrew Univ., Jerusalem, Israel). *Anal. Chim. Acta*, 1959, **20** (3), 216–227.—Procedures are given for the determination, in $\simeq 10$ min., of $Au^{III}$ ($\simeq 1$ mg), $Pd^{II}$ ($\Rightarrow 0{\cdot}5$ mg) and $Pt^{IV}$ ($\simeq 1{\cdot}5$ mg), either alone or in mixtures, by heterometric titration with 0·01 *M* nitron soln. at pH 1 to 7 in the presence of an excess of KSCN. The sample soln. ($\simeq 20$ ml) can contain HCl, $HNO_3$, $H_3PO_4$ or acetic acid as well as any of the following masking agents in excess—citrate, tartrate, EDTA (disodium salt), $P_2O_7^{4-}$ and $P_3O_{10}^{5-}$. The error is < 1%. The insol. compounds obtained quant. at the end-points of the titrations are $AuN$, $Au_2N_3$, $Pd_2N_3$ and $Pt_4N_3$ ($N$ = nitron). When determining Au, the sensitivity is increased if the heterometric titration is made in a soln. containing a large excess of aq. $NH_3$ ($\simeq 0{\cdot}3$ *M*), the end-point occurring at $Au_2N_3$. W. J. BAKER

4796. **Spectrophotometric determination of osmium with 1-naphthylamine-4:6:8-trisulphonic acid.** E. L. Steele and J. H. Yoe (Dept. of Chem., Univ., Charlottesville, Va., U.S.A.). *Anal. Chim. Acta*, 1959, **20** (3), 205–211.—From 0·1 to 6·5 p.p.m. of Os can be accurately determined by measuring the extinction at 555 m$\mu$ of the stable violet complex formed at pH 1 to 1·5 (dil. HCl) when aq. 1-naphthylamine-4:6:8-trisulphonic acid soln. ($5 \times 10^{-4}$ *M*) is warmed for $\simeq 45$ min. at 40° with the soln. of osmate. Beer's law is obeyed and the complex has a composition of 2 moles of reagent to 1 mole of $Os^{VI}$. Since many common ions interfere, an initial separation of Os should be made by distillation from $HNO_3$ soln. into 0·05 *N* KOH before applying the spectrophotometric procedure. W. J. BAKER

4797. **Tracer investigation of iridium - platinum separation by anion exchange.** D. D. Busch, J. M. Prospero and R. A. Naumann (Princeton University, N.J.). *Anal. Chem.*, 1959, **31** (5), 884–886.—Rapid separation of Ir from Pt (10 mg of each) is achieved on Dowex A-1 anion-exchange resin, as shown by tracers ($^{192}Ir$, $^{191}Pt$ and $^{193}Pt$). The metals are converted into $MCl_6^{2-}$ and reduction with hydroxyammonium chloride then produces $IrCl_6^{3-}$; 3% of the Pt is also reduced and eluted with the Ir and 0·5% is lost on the column. The purity of the Pt recovered is >99%. Thus $^{188}Ir$ can readily be separated from its parent, $^{188}Pt$. *Procedure*—Add conc. HCl (2 ml) to the soln. containing 10 mg each of Pt and Ir. Evaporate just to dryness, add 9 *N* HCl (2 ml) and 30% $H_2O_2$ soln. (2 ml), and again evaporate just to dryness. Add 3 *N* HCl (1 ml) and 10% hydroxyammonium chloride soln. (5 drops), heat for 3 min., and transfer the soln. to the Dowex column at 80°. Elute the $IrCl_6^{3-}$ with 9 *N* HCl and the $PtCl_6^{2-}$ with 50% $HClO_4$. J. P. STERN

4798. **Sampling and analysis of bubbles in glass by mass spectrometry.** J. C. Neerman and F. R. Bryan (Sci. Lab., Ford Motor Co., Dearborn, Mich.). *Anal. Chem.*, 1959, **31** (4, Part I), 532–535.—The gas content in bubbles ranges from 0·01 to 2 $\mu$l-atm. at 25°; relative concn. in the upper range can be determined to within 1 or 2%, and absolute values (down to 0·05 $\mu$l) to within 10% of the true value. Samples $\frac{7}{16}$ in. square and $\Rightarrow \frac{1}{8}$ in. thick are used for the test. The bubble breaker consists of a modified stainless-steel bellows valve, with a pointed steel end-piece attached to the valve plunger, and is connected through two valves to the spectrometer analyser tube inlet and the spectrometer vacuum system, respectively. Detailed instructions for operation are given, including those for the blank determination. Carbon dioxide, N, $SO_2$, A and O were identified; the presence of CO and $H_2O$ was not confirmed. Pure compounds are used for calibration. P. D. PARR-RICHARD

4799. **Rational analysis of fireclays.** W. E. Worrall (Brit. Ceramic Res. Ass., Queens Rd., Penkhull, Stoke-on-Trent). *Trans. Brit. Ceram. Soc.*, 1959, **58**, 145–153.—A Yorkshire fireclay was separated into 7 fractions of particle size from 0·075 to > 36 $\mu$ and analysed. The conventional methods of calculating the rational analysis on the assumptions that the fireclay mineral is kaolinite and that the alkalis are present as felspar or mica are shown to be unsound. A new method is based on the "combined $H_2O$" content (corrected for organic matter and carbonate) for the computation of the clay mineral. It is shown that the clay mineral in fireclays has a lower $Al_2O_3$ content than kaolinite, the deficiency being made up by the substitution of $Fe_2O_3$ and MgO. An approx. formula for the clay mineral is given, which gives more consistent results. J. A. SUGDEN

4800. **Chemical methods of phase analysis of metal - ceramic alloys [alloys used for cermets] based on titanium carbide and chromium and titanium diborides.** N. M. Popova, A. F. Platonova and L. V. Zaslavskaya. *Zavod. Lab.*, 1959, **25** (3), 271–273.—Various methods applied to the powdered material (270 mesh) are described. With titanium carbide, boiling with HCl leaves the carbide unattacked, but Ni, Co, Cr and Fe, with $\Rightarrow 0{\cdot}1\%$ of Ti, dissolve. The carbide phase contains Cr but not Ni and Co. Metallic Nb can be extracted by boiling with HF but its carbide, together with that of Ti, is unattacked. The phase analysis of titanium carbide for Mo is carried out by electrochemical dissolution in 5% NaOH soln. Methods of studying the borides of Ti and Cr are also described. G. S. SMITH

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*See also Abstracts*—**4659**, Mercaptosuccinic acid in inorganic analysis. **4665**, Use of separating columns in analysis. **4874**, Determination of mercury in biological material. **4875**, Determination of Tl. **4877**, Determination of Cr in blood. **4980**, Determination of nitrogen oxides in air. **4989**, Determination of Mo in water. **4997**, Determination of Mo in plants. **5029**, Use of $Ag^{131}I$ in chromatography of phosphoric acids. **5039**, Detection of Mn in aluminium. **5051**, **5052**, Determination of O in gases. **5056**, Thermogravimetry of sulphates and chlorides. **5059**, Determination of impurities in bismuth. **5061**, Determinations of traces of Cd, Pb, Bi and Zn.

## 3.—ORGANIC ANALYSIS

*Determination of elements and radicals and of organic compounds not included in other sections. Organic industrial products, including petroleum and its products, fuels, detergents, volatile oils, cosmetics, dyestuffs, fibres, plastics, resins, paints, elastomers, leather, explosives, etc.*

4801. **Analysis for industry [absorption of nitrogen oxides in carbon and hydrogen analyses].** A. M. G. Macdonald. *Ind. Chemist*, 1959, **35**, 193–195.—A review is presented, in which inorganic absorbents (*e.g.*, $MnO_2$, $PbO_2$, Cu and soln. of oxidants in conc. $H_2SO_4$) and other absorbents (*e.g.*, aminoazobenzene, diphenylamine, sulphamic acid, ammonium sulphamate and trihydroxyammonium phosphate) are critically discussed and compared. It is suggested that suitably prepared $MnO_2$ yields accurate results, has a high absorptive capacity and is free from troubles in routine analysis.

S. C. I. Abstr.

4802. **Determination of nitrogen in some heterocyclic compounds.** I. Čepčiansky and L. Chromcová (School of Chem. Technol., Prague). *Chem. Průmysl*, 1959, **9** (4), 188–190.—A new modification of Kjeldahl's method based on the use of a mixture of $H_2SO_4$, $H_3PO_4$, $CuSO_4$ and Se for the mineralisation of the sample permits the determination of N in isatin and its derivatives (4-chloro-7-methoxyisatin and 4-bromo-7-methylisatin), and in benzotriazole, 1-phenylbenzotriazole and 2-phenylbenzotriazole and their substitution derivatives. Divide a mixture of 3 vol. of $H_2SO_4$ (96%) and 1 vol. of $H_3PO_4$ (65%) into two equal parts; to the first add $CuSO_4.5H_2O$ (1 g per 100 ml of mixed acids), to the second add powdered Se (1 g per 100 ml of mixed acids); dissolve both mixtures separately by heating, cool, combine and heat to boiling. For 0·1 to 0·15 g of sample, 15 to 22 ml of the digestion mixture is recommended. J. Zýka

4803. **Simultaneous micro-determination of nitrogen and of chlorine and bromine in organic compounds.** A. Konovalov (Univ., Louvain). *Ind. Chim. Belge*, 1959, **24** (3), 259–262.—*Procedure*—The weighed sample (1 to 5 mg) is placed in a distilling flask with 100 ml of water and 2 ml of 30% KOH soln. and a glass bead. The delivery tube is arranged to be 1 mm from the surface of the liquid in the receiver (a 250-ml flask containing 20 ml of water and 2 to 5 ml of 0·02 *N* HCl). The liquid in the flask is distilled quietly (1 hr.) until the vol. is reduced to 2 ml. The excess of acid in the receiver is titrated with 0·02 *N* NaOH, with 5 drops of Tashiro indicator (2 ml of 1% aq. methylene blue and 100 ml of 0·04% methyl red in 50% ethanol). The residue from the distillation is washed out into a Berlin flask with 10 ml of water, and 2 ml of 3% $H_2O_2$ is added to convert chlorate or bromate into halide, and the soln. is boiled down to 10 ml to destroy excess of $H_2O_2$. The liquid is neutralised to phenolphthalein with aq. $HNO_3$ (1:2) and 2 ml in excess is added. An excess of 0·01 *N* $AgNO_3$ is added and the soln. is filtered through a medium comprising a layer of asbestos (washed with $HNO_3$) covered with 1·5 cm of sea sand and 0·5 cm of cotton wool. To the clear filtrate are added 1 ml of 0·5% starch soln. and 8 drops of 0·02 *N* ethanolic iodine, and the excess of $AgNO_3$ in this colourless soln. is titrated with 0·01 *N* KI to a blue colour. Results are given for 18 compounds, including acid amides, cyanides, amine hydrochlorides and bromine derivatives of acid amides and cyanides. E. J. H. Birch

4804. **Rapid micro-analytical method for the determination of phosphorus and for the simultaneous determination of phosphorus and halogens in organic substances.** W. Merz (Badischen Anilin- & Soda-Fabrik A.-G., Ludwigshafen/Rhein, Germany). *Mikrochim. Acta*, 1959, (3), 456–465.—The sample (3 to 8 mg according to the expected P and halogen content) is wrapped in ashless filter-paper and burned in an oxygen-filled Erlenmeyer flask as recommended by Schöniger (*cf. Anal. Abstr.*, 1955, **2**, 1816). The combustion products are absorbed in a suitable soln. and the $Cl^-$ or $Br^-$ content is determined by the Vieböck method (*Ber.*, 1932, **65**, 496), and $I^-$ by the Leipert method (*Biochem. Z.*, 1933, **261**, 436). The determination of P is carried out photometrically, with the molybdenum blue reaction suitably modified for routine use. An accuracy of $\simeq \pm$ 0·2% is attainable for the P determination and a similar accuracy for the simultaneous determination of P and halogens. The method may be used for semi-micro determinations without modification.

D. F. Phillips

4805. **Gravimetric semi-micro determination of phosphorus as quinoline molybdophosphate in organic compounds.** T. R. F. W. Fennell and J. R. Webb (Royal Aircraft Estab., Farnborough, Hants, England). *Talanta*, 1959, **2** (2), 105–108.—The quinoline molybdophosphate finish is applied to the semi-micro determination of P following fusion with $Na_2O_2$ (Fennell *et al.*, *Analyst*, 1957, **82**, 639). Drying at 110° causes no decomposition of the ppt., and the theoretical factor (0·01400) is applicable for calculating the P content. Errors due to the presence of 1·5 g of NaCl and 0·02 g of $F^-$ as NaF are insignificant on the semi-micro scale. A two-crucible weighing technique is described which minimises errors due to the hygroscopicity of the ppt. A second method, in which only the working crucible is dried and weighed against a tare, gives only insignificant errors. A third rapid method, in which the crucible after washing is wiped externally, and the ppt. washed with dioxan (3 × 2 ml) and dry diethyl ether (3 × 2 ml) and dried by air suction, is also described. The solvents caused no loss of ppt. It is suggested that the finish could also be used after wet-oxidation or oxygen-flask procedures.

R. E. Essery

4806. **Thermochromic detection of the acetonyl grouping in organic compounds.** E. Sawicki (R. A. Taft San. Engng Center, U.S. Dept. of Health, Education and Welfare, Cincinnati, Ohio, U.S.A.). *Chemist Analyst*, 1959, **48** (1), 4–5.—To 0·1 ml of a methanolic test soln. add 0·5 ml of a 0·5% methanolic soln. of 2-hydroxy-1-naphthaldehyde. Gently agitate the mixture with a stream of HCl gas for 30 sec. Add 0·5 ml of *o*-dichlorobenzene, and boil the mixture vigorously till all the methanol, but none of the dichlorobenzene, has distilled off. Cool the remaining liquid to room temp. A reversible change from a yellow, pink or pale-green colour at the boiling-point to a brilliant green at room temp. indicates a positive reaction. Aliphatic ketones containing the $CH_3.COCH_2$– group give a sensitive and specific reaction, the only exceptions being *cyclo*butanone, *cyclo*pentanone and *cyclo*hexanone, which also give a green colour. Other types of carbonyl compounds do not react. The sensitivities for 15 compounds

ranged from 0·2 to 5 μg (phenylpropanone 100 μg). The chemistry of the reaction is discussed.
R. E. ESSERY

4807. **Determination of straight chains [-$(CH_2)_n$-] of different lengths by infra-red absorption spectroscopy.** A. V. Iogansen (All-Union Sci. Res. Inst. of the Petroleum Ind.). *Zavod. Lab.*, 1959, **25** (3), 302–303.—Saturated hydrocarbons show characteristic bands in the range 720 to 780 $cm^{-1}$. The non-branching chains can be sub-divided into five structural groups according to the value of $n$ in the chain $-(CH_2)_n-$, thus, (*i*) $n = \not< 6$, (*ii*) $n = 4$ or 5, (*iii*) $n = 3$, (*iv*) $n = 2$, and (*v*) $n = 1$, each of which is characterised by absorption bands of definite frequency, intensity and width. The spectrum of any saturated hydrocarbon can be considered as a superposition of these bands with weights proportional to their relative concn. The analysis according to these structural groups can be carried out in the same way as for a five-component mixture. Group (*v*) is determined from absorption at 782 $cm^{-1}$, the other four groups show mutual superposition and can be determined by taking measurements at the four points 721, 724·5, 728 and 739 $cm^{-1}$ and solving four simultaneous equations. Examples of the use of the method and confirmation of its validity are given.
G. S. SMITH

4808. **Determination of isoprene in reaction mixtures.** M. Kubínová (Res. Inst. Synth. Rubber, Gottwaldov, Czechoslovakia). *Chem. Průmysl*, 1959, **9** (3), 160–164.—A new chromatographic method based on the absorption of isoprene in maleic anhydride has been developed and compared with a colorimetric method based on the formation of a yellow complex after treating the sample with mercuric acetate in anhyd. methanol. It is stated that the chromatographic method gives more precise results over the whole concn. range of the analysed sample. The successful separation of $C_5$ hydrocarbons has been achieved in a 3-metre column filled with kieselguhr impregnated with ethyl oxo*cyclo*pentanecarboxylate, with H as carrier gas. The method is suitable for mixtures boiling at $\not< 40°$.
J. ZÝKA

4809. **Analysis of contact gas [formed in the catalytic dehydrogenation of butane, etc.] by a chromatographic method.** V. A. Kolobikhin. *Zavod. Lab.*, 1959, **25** (2), 154–157.—Mixtures of $CO_2$, H, $CH_4$, $C_2H_6$, $C_2H_4$, $C_3H_6$, $C_3H_8$, $C_4H_{10}$ and $C_4H_8$ are separated and determined by use of heated columns.
G. S. SMITH

4810. **Semi-micro method for the characterisation and determination of carbon tetrachloride.** P. Blanc, —. Godfrain and R. Lescure. *Chim. Anal.*, 1959, **41** (2), 54–55.—The method depends on the production of a rose-red colour on treatment of $CCl_4$ with thymol and copper in alkaline soln. Reagent *A* [100 ml of NaOH soln. (36° Bé) and 10 ml of 5% aq. $CuSO_4$ soln.] (2 ml) is placed in a test-tube (diam. 20 mm) and reagent *B* (5 g of cryst. thymol in 100 ml of 95° ethanol) (2 ml) is added without mixing, followed by 1 ml of a soln. of the sample in 95° ethanol. The tube is fitted with a reflux condenser and immersed in a boiling-water bath for 5 min. After rapid cooling the two phases separate, the alcoholic layer developing a rose-red coloration, the intensity of which depends on the concn. of $CCl_4$. The reaction is sensitive (1 in $2·5 \times 10^4$) and specific, but the presence of acids, even in the atmosphere, causes interference.
S. M. MARSH

4811. **Colorimetric determination of 2-ethylhexane-1:3-diol.** M. C. Bowman, M. Beroza and F. Acree, jun. (Entomology Res. Div., Agric. Res. Service, U.S. Dept. of Agric., Orlando, Fla.). *J. Agric. Food Chem.*, 1959, **7** (4), 259–261.—*Procedure*—Dilute aliquots (containing 0 to 105 μg) of a standard aq. soln. of 2-ethylhexane-1:3-diol (**I**) (52·5 μg per ml) in stoppered tubes to 2 ml with water, cool in ice, and keep cool during the addition of 4 ml of reagent [freshly prepared 0·2% (w/v) soln. of *p*-dimethylaminobenzaldehyde in conc. $H_2SO_4$]. Heat the tube in boiling water (stoppering tightly when warm) for 60 min., cool in ice for 5 min. and, after 30 min. at 25°, measure the extinction of each soln. at 500 mμ against water. Plot the extinctions (corrected for the reagent blank) against concn. For the determination of the insect repellent on glass, cloth or skin, wash the area with sufficient re-distilled ethanol (95%) to effect complete extraction and dilute a suitable aliquot with enough water to bring the concn. of **I** within the range covered by the standard curve, and the concn. of ethanol to $\not> 5\%$. Develop the colour in a suitable aliquot of the diluted soln. as in the preparation of the standard curve.
S. C. JOLLY

4812. **Analysis of dilute aqueous glycerol solutions with quinquevalent vanadium.** D. M. West and D. A. Skoog (Stanford Univ., Calif., U.S.A.). *Anal. Chem.*, 1959, **31** (4, Part I), 586–588.—The method is based on the oxidation of glycerol to formic acid by an acidic soln. of $V^V$, the excess of reagent being back-titrated with a $Fe^{2+}$ soln., with N-phenylanthranilic acid as indicator. Results are accurate to within ±3% in the concn. range 4 to 34 mg of glycerol and compare favourably with those of other methods based on oxidation.
G. P. COOK

4813. **The Molisch reaction.** T. A. Turney (Chem. Dept., Univ. of Auckland, Auckland, New Zealand). *Analyst*, 1959, **84**, 194.—The utility of the Molisch reaction can be extended if it is applied by adding 0·1 g of the sample to 0·1 g of 1-naphthol in a dry test-tube, then adding 2 ml of conc. $H_2SO_4$ and mixing. A violet or red - violet colour forming slowly indicates the presence of a compound having a cyclic ketol group, *e.g.*, a pentose, hexose, polysaccharide or glycoside.
A. O. JONES

4814. **Improved method for determination of reducing substances [carbohydrates].** V. M. Kats and M. I. Sholkhet. *Sakhar. Prom.*, 1959, (2), 35.—Fehling's soln. No. 2 is replaced by a soln. containing 128 g of trihydroxyglutaric acid and 207 g of NaOH in 1 litre. The procedure remains the same as for the Bertrand method. The quantity of reducing sugars is $kt$, where $k = 0·6068$, 0·6027, 0·6047 and 0·9383 for glucose, fructose, invert sugar and maltose, respectively, and $t$ is the amount of Cu in the copper oxide ppt.
SUGAR IND. ABSTR.

4815. **Use of 4:5-dinitroveratrole for the ultramicro determination of reducing sugars on paper chromatograms by a reflectance method.** A. Bevenue and K. T. Williams (W. Utilisation Res. and Devel. Div., Agric. Res. Service, U.S. Dept. of Agric., Albany, Calif.). *J. Chromatography*, 1959, **2** (2), 199–201.—The chromatogram is dipped in a 1% soln. of 4:5-dinitroveratrole in acetone, dried and then dipped in *N* KOH in 95% ethanol.

The colour is developed by heating at 60° for 10 min. in a humid atmosphere and is then measured on the paper with a reflectance photometer at 515 mμ. The plot of extinction *vs.* concn. of sugar is linear over the range 2 to 20 μg for fructose, glucose and arabinose. W. T. CARTER

4816. **The hydrolysis of oligosaccharides with regard to their reductimetric determination.** K. Täufel and H. Ruttloff (Inst. Ernährung, Potsdam-Rehbrücke, Berlin, Germany). *Ernährungsforschung*, 1959, **4** (1), 44–52.—The extent and rate of hydrolysis of sucrose, lactose, maltose and raffinose by hydrochloric and citric acids are studied by means of paper chromatography. The formation of transglycosidation products, under acid conditions, is shown on the chromatograms when the solutions are chromatographed without prior neutralisation. J. V. RUSSO

4817. **Paper chromatography of 2:4-dinitrophenylhydrazones. Resolution of alkan-2-one, *n*-alkanal, alk-2-enal and alka-2:4-dienal derivatives.** A. M. Gaddis and R. Ellis (Dairy and Meat Lab., U.S. Dept. of Agric., Beltsville, Md.). *Anal. Chem.*, 1959, **31** (5), 870–875.—These derivatives with chain lengths up to $C_{14}$ can be separated into their homologous classes by ascending chromatography on untreated paper, with light petroleum (boiling-range 37° to 40°) as solvent. The individual components of each class can then be separated by known chromatographic methods. $R_F$ values are given. All the derivatives can be identified except those of acetone, acetaldehyde, propionaldehyde, butyraldehyde and acraldehyde. G. BURGER

4818. **Separation and identification of *n*-alkanals, alkan-2-ones, alk-2-enals and alka-2:4-dienals by paper chromatography and direct spectrophotometric examination.** M. Nonaka, E. L. Pippen and G. F. Bailey (Agric. Res. Service, U.S. Dept. of Agric., Albany, Calif., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 875–877.—These compounds can be separated by descending chromatography of their 2:4-dinitrophenylhydrazones dissolved in $CHCl_3$ on paper impregnated with a soln. of 2-phenoxyethanol in acetone. The developing solvent is *n*-heptane. *R* values are referred to the *n*-heptaldehyde derivative. The spots are cut out and the absorption spectra examined in the range 300 mμ to 450 mμ. In the chromatogram, compounds of the same homologous series are separated but overlap with those of a different series and different chain length. As each homologous series has a characteristic absorption max., the individual compounds can be identified. Care is necessary with unknown mixtures, as compounds outside the classes studied may cause interference. G. BURGER

4819. **Simultaneous determination of formaldehyde and paraformaldehyde.** Z. Bellen (Anal. Dept., Inst. of Gen. Chem., Warsaw). *Chem. Anal., Warsaw*, 1959, **4** (1–2), 13–18.—The main difficulty is due to the decomposition or depolymerisation of paraformaldehyde in the presence of $H_2O$, which reaches a maximum at pH 4 to 5 and 0°. The recommended method is based on the condensation of dimedone with formaldehyde, the resulting compound being pptd. in acetate buffer at pH 4·6, filtered off and determined by titration with standard NaOH soln., without decomposition of paraformaldehyde. The sum of free formaldehyde and polymers is determined by oxidation with iodine in alkaline soln., acidifying and titrating the excess of iodine with $Na_2S_2O_3$ soln. in the presence of starch. The content of paraformaldehyde is obtained by difference. W. B. MIASKOWSKI

4820. **Analysis of formaldehyde. Proposed revision of TAPPI standard T600m-45.** *TAPPI*, 1958, **41**, 170A–171A.—The method is essentially the same as those of the U.S.P. and of the A.O.A.C., the major change being the introduction of bromothymol blue as an alternative indicator, which gives a sharper end-point than litmus. To 50 ml of *N* NaOH add 50 ml of $H_2O_2$ (3%) and approx. 3 ml of formaldehyde soln. weighed accurately with a weight pipette. Place a funnel in the neck of the flask, heat on a steam bath for 5 min. with shaking, cool and titrate the excess of NaOH with *N* HCl or $H_2SO_4$, with bromothymol blue or litmus as indicator. The acidity of the formaldehyde is corrected for by a separate titration of 3 ml with NaOH soln. without $H_2O_2$. The titration of formaldehyde in $Na_2SO_3$ soln. with $H_2SO_4$, with aurin as indicator, is recommended for control purposes. R. AICHER

4821. **Determination of aldehydes by the argentimetric method. I. Determination of formaldehyde in technical hexamine.** Z. Bellen and B. Sękowska (Anal. Depart., Inst. of Gen. Chem., Warsaw). *Chem. Anal., Warsaw*, 1959, **4** (1–2), 25–28.—The method is based on the oxidation of formaldehyde by means of Tollens reagent prepared from a known quantity of $AgNO_3$ and the potentiometric titration of $Ag^+$ with a standard soln. of KI. Under these conditions hexamine does not undergo decomposition into formaldehyde and ammonia. The method is sufficiently accurate for technical purposes. W. B. MIASKOWSKI

4822. **Bromimetric determination of acraldehyde in aqueous medium.** J. Młodecka (Anal. Dept., Inst. of Gen. Chem., Warsaw). *Chem. Anal., Warsaw*, 1959, **4** (1–2), 53–58.—The method is designed for visual or electrometric determinations in aq. soln., and is based on the titration of a known volume of acidified bromate - bromide soln., standardised with pure acraldehyde, with the test soln. in a closed flask. The end-point is determined either potentiometrically by the dead-stop method or visually by the red colour of methyl orange, added at the moment of the discharge of the bromine colour. The method is short and simple, but speed is essential, since the soln. of acraldehyde is unstable. The error is $\simeq$ 1·5%. W. B. MIASKOWSKI

4823. **Analytical chemistry of the aldehydes. II. Iodimetric procedure for the direct determination of glyoxal by means of its bisulphite compound.** E. Schulek and L. Maros (L. Eötvös Univ., Budapest). *Acta Chim. Acad. Sci. Hung.*, 1959, **19** (4), 473–478 (in German).—The glyoxal is converted into its bisulphite compound by adding it in aq. soln. (10 ml, $\simeq$0·1%) to an excess of $Na_2SO_3$ soln. (5%) (3 ml) made slightly acid to methyl red with acetic acid. The mixture is covered with a layer of pentane and set aside for 30 min. The excess of $SO_2$ is then removed with iodine, and 2 ml of hydroxyammonium chloride soln. and 5 ml of 20% NaOH soln. are added. After 5 min. the mixture is neutralised with 20% HCl soln., 2 ml is added in excess, and the liberated $H_2SO_3$ is titrated with 0·1 *N* iodine. G. BURGER

4824. **Determination of acetone and ethyl methyl ketone in the presence of aldehydes.** L. N. Petrova, E. N. Novikova and A. B. Skvortsova. *Zhur. Prikl. Khim.*, 1959, **32** (6), 1407–1409.—The method of oxime formation can be used if there is a preliminary reaction with aniline to convert aldehydes into non-volatile Schiff bases. *Procedure*—Heat the distillation flask containing $\simeq 0{\cdot}5$ g of an aldehyde - acetone or aldehyde - ethyl methyl ketone mixture and a 15% soln. (5 ml) of aniline in benzene to 50° to 60°; gradually raise the temp. of the paraffin bath to 150°. Collect the distillate in a $0{\cdot}5\ N$ hydroxyammonium chloride soln. (20 ml) in 80% ethanol and, after washing the condenser with ethanol or methanol (15 ml) without disconnecting the apparatus, titrate the HCl in the receiver with a $0{\cdot}5\ N$ ethanolic KOH soln. to bromophenol blue. Determine the amount of aniline distilled over with the benzene in the absence of the test mixture. The presence of $H_2O$, alcohols, ethers and acids in the test mixture does not affect the determination. K. R. C.

4825. **Colorimetric determination of *n*-amyl ethyl ketone with 3:5-dinitrobenzoic acid.** D. H. E. Tattje and C. Scholtens (Lab. Farm. Galen. Farm., Rijksuniv., Groningen, Holland). *Pharm. Weekbl.*, 1959, **94** (5), 137–142.—An ethanolic soln. (4 ml containing $\gtrsim$ 12 mg of the ketone) is mixed at 20° with 5 ml of an ethanolic 4% (w/v) soln. of the acid, followed by 2 ml of $3{\cdot}5\ N$ NaOH. The colour intensity is measured after 20 min. in a 0·5-cm cell at 545 mμ against a freshly prepared blank. The calibration graph is linear. Values obtained for saponified lavandin and lavender oils are in good agreement with those obtained by the hydroxyammonium chloride method, and show better reproducibility. Values determined directly on the oils are (unaccountably) 50 to 300% higher than those given by the hydroxyammonium chloride method. Cineole, linalol and D-camphor do not react with the acid. P. S. Arup

4826. **Paper-chromatographic identification of organic acids resulting from fermentations.** A. D. Panek (Lab. of Microbiol., Inst. of Chem., Univ. of Brazil, Rio de Janeiro). *J. Chromatography*, 1959, **2** (2), 211–213.—The mixtures of acids were separated by ascending chromatography on Whatman No. 1 paper, with *n*-propanol - conc. aq. $NH_3$ (7:3) as solvent (*cf.* Isherwood and Hanes, *Anal. Abstr.*, 1954, **1**, 314). After development for 7 hr. the spots were detected by being sprayed with ethanolic bromocresol green soln. and heated at 80° for 10 min. Results are given for the examination of mashes from alcoholic, lactic, acetic and citric fermentations. W. T. Carter

4827. **Automatic derivative potentiometric and spectrophotometric titrations of organic acids.** H. V. Malmstadt and D. A. Vassallo (Univ. of Illinois, Urbana, U.S.A.). *Anal. Chem.*, 1959, **31** (5), 862–865.—Carboxylic acids, sulphonamides, imides, thiols, phenols and enols dissolved in any solvent mixture containing $\lesssim$ 90% of acetone can be titrated with tri-*n*-butylmethylammonium hydroxide. The end-point may be detected by derivative potentiometry or spectrophotometry. Of the electrode combinations tried, none showed any advantage over platinum and graphite (from a 9H pencil). A table of indicators is given for the spectrophotometric method. These indicators can also be used for visual end-point detection. The potentiometric method is not suitable for very weakly acidic materials (*e.g.*, phenol). The precision of each method is within the burette-reading error. G. Burger

4828. **Oxidation of some organic compounds with standard solutions of quinquevalent vanadium.** D. M. West and D. A. Skoog (Stanford Univ., Calif., U.S.A.). *Anal. Chem.*, 1959, **31** (4, Part I), 583–586.—α-Hydroxy acids appear to react stoicheiometrically with an acidic soln. of $V^V$, the products being $CO_2$ and the corresponding carboxylic acid with one C atom less than the original substance. The excess of vanadate is back-titrated with $(NH_4)_2SO_4.FeSO_4.6H_2O$ soln., with N-phenylanthranilic acid as indicator. The relative error is $< 1\%$ for lactic acid in the concn. range of 9 to 70 mg. G. P. Cook

4829. **Analysis of high-molecular-weight quaternary ammonium chlorides.** M. Babcock, D. E. Terry and A. J. Milun (Chem. Lab., Gen. Mills Inc., Minneapolis, Minn., U.S.A.). *J. Amer. Oil Chem. Soc.*, 1959, **36** (3), 93–94.—The method is applicable to the determination of quaternary ammonium chloride, amine hydrochloride (or free alkali) and NaCl in commercial products. *Amine hydrochloride*—The sample (1 to 2 g) is dissolved in 50 ml of ethanol - toluene (1:1) and titrated with either $0{\cdot}05\ N$ NaOH, or $0{\cdot}5\ N$ HCl for free alkali, with phenolphthalein as indicator. *Amine*—The sample (2 g) is dissolved in 50 ml of ethanol and titrated with $0{\cdot}2\ N$ HCl, with bromocresol green as indicator. *NaCl (in the absence of free alkali)*—The sample (1 to 2 g) is ignited, and the residue is extracted with 5 to 10 ml of water. The extract is warmed, then diluted with 10 to 15 ml of water, and the soln. titrated with $0{\cdot}1\ N$ $AgNO_3$, with dichlorofluorescein as indicator. *Quaternary ammonium chloride*—The sample (1 g) is dissolved by warming with 50 ml of *iso*propyl alcohol, dichlorofluorescein soln. is added and the soln. is titrated with $0{\cdot}1\ N$ $AgNO_3$. G. R. Whalley

4830. **Determination of nitrite in quaternary ammonium nitrites.** J. V. Killheffer, jun., and E. Jungermann (Armour Chem. Div., Chicago, Ill., U.S.A.). *Anal. Chem.*, 1959, **31** (4, Part I), 581–582.—Nitrite ions are oxidised to $NO_3^-$ with chloramine T, the excess of which is determined iodimetrically. Dimethylformamide is used as solvent. The precision is approx. $\pm 0{\cdot}3\%$ and recoveries from pure compounds are 99·8 to 100·2%. G. P. Cook

4831. **Mass-spectrometric analysis of aliphatic amides.** J. A. Gilpin (Dow Chemical Co., Midland, Mich., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 935–939.—The mass spectra of 35 aliphatic amides have been tabulated and correlated. Fragmentation and re-arrangement ions characteristic of primary, secondary and tertiary amides are noted as well as spectral characteristics common to all three groups. Rules are given for the interpretation of the spectra and the identification of pure amides. G. Burger

4832. **Infra-red and ultra-violet spectra of ethylnitrolic acid and its sodium salt.** D. J. Morgan (British Nylon Spinners Ltd., Pontypool, Mon., Wales). *J. Appl. Chem.*, 1959, **9** (4), 201–203.—The infra-red spectra of ethylnitrolic and *n*-propylnitrolic acid are recorded together with the u.v. spectra of the former and its sodium salt. It is concluded that the ethylnitrolic acid molecule

contains a nitro and an azomethine group and is strongly hydrogen-bonded. Nitrous oxide, $NaNO_2$ and Na acetate are identified among the dissociation products of the apparently mesomeric sodium salt. F. J. M.

4833. **New method for the identification of volatile thiols by paper chromatography.** A. Jacot-Guillarmod and P. Ceschini (Batelle Mem. Inst., Geneva, Switzerland). *Helv. Chim. Acta*, 1959, **42** (3), 713–715 (in French).—Alkylthiols ($CH_3$ to $C_5H_{11}$) are identified by descending paper chromatography of the 2:4-dinitrophenylhydrazones of their 3-alkylthiopropionaldehydes, which are formed by the reaction of the thiols with acraldehyde. The stationary phase is dimethylformamide and the mobile phase *cyclo*hexane saturated with dimethylformamide. $R_F$ values are given. G. P. Cook

4834. **Titrimetric determination of alkyl mercaptan [alkane thiol] - dialkyl sulphide and alkyl mercaptan - alkyl disulphide mixtures.** B. Jaselskis (Univ. of Michigan, Ann Arbor, U.S.A.). *Anal. Chem.*, 1959, **31** (5), 928–931.—*Procedure for mixtures of an alkane thiol and a dialkyl sulphide*—Two equal aliquots are diluted with ethanol. One is acidified and titrated for thiol with iodine soln. The other is made alkaline and vinyl cyanide is added. This soln. is acidified and titrated with $KBrO_3$ - KBr soln. The dialkyl sulphide content is calculated from the two titrations. *Procedure for mixtures of an alkane thiol and an alkyl disulphide*—One aliquot is titrated with iodine soln. The other is reduced by heating under reflux with zinc in a mixture of ethanol, acetic acid and HCl, and titrated with iodine soln. This method is not applicable to tertiary alkyl disulphides. The error is $< 1\%$. G. Burger

4835. **Resolution of isomeric xylenes by gas - liquid chromatography.** Z. Zlatkis, Su-Yu Ling and H. R. Kaufman (Univ. of Houston, Tex., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 945–947.—The xylene isomers can be separated on a stationary phase of 1-chloronaphthalene, dimethylsulpholane or a mixture of ethylene carbonate and 1-nitronaphthalene if one of these liquids is supported on fire-brick which has been treated with aqua regia. The brick is heated with aqua regia for 1 hr., washed with $H_2O$, dil. aq. NaOH soln. and $H_2O$ again, dried and screened. Chromosorb can be used when treated in the same way. The use of such specially treated fire-brick results in improved resolution, enables finer mesh sizes and longer columns to be employed, and reduces pressure drop across the column. G. Burger

4836. **Infra-red absorptiometric determination of isomers of xylene and ethylbenzene in their mixtures.** T. Kraczkiewicz-Biernacka and B. Kontnik (Dept. of Tech. Physics, Inst. of Gen. Chem., Warsaw). *Chem. Anal., Warsaw*, 1959, **4** (1–2), 97–104.—A new method for the determination of a quaternary mixture of *o*-, *m*- and *p*-xylenes and ethylbenzene by i.r. absorption has been developed. The analytical bands used were—8·950 $\mu$, 10·175 $\mu$, 11·425 $\mu$ and 10·375 $\mu$ for *p*-, *o*- and *m*-xylenes and for ethylbenzene, respectively, and the respective errors of determination were $\simeq$ 0·6%, 0·3%, 2·6% and 6·3%. A method of successive approximation was used for calculation. *p*-Xylene in the presence of other isomers of xylene can be simply and rapidly determined by the application of the base line method, with *cyclo*hexane as solvent, with a possible relative error of 2%. W. B. Miaskowski

4837. **Application of quantitative molecular spectrographic analysis to certain stages in the production of phenol and acetone [from *iso*propylbenzene hydroperoxide].** N. K. Rudnevskii and V. V. Zharkov (Gorki State Univ.). *Zavod. Lab.*, 1959, **25** (3), 297–298.—The determination by i.r. absorption of *iso*propylbenzene hydroperoxide, 2-phenylpropan-2-ol and acetophenone in technical hydroperoxide is described. G. S. Smith

4838. **High-frequency conductimetric titration of weak acids.** G. R. Jamieson (Chem. Dept., Tech. Coll., Paisley, Scotland). *J. Appl. Chem.*, 1959, **9** (4), 209–212.—The conductimetric titration of phenols, enols and imides, in aq. soln., with LiOH soln. and a high-frequency titrimeter is described. Typical titration plots obtained by both direct titration with alkali and back-titration of an excess of hydroxide with standard HCl soln. show sharp breaks at the end-points, and satisfactory results for monohydric phenols, etc., by both procedures are tabulated. Dihydric and trihydric phenols give a curve with two breaks, only one of which is sharp enough for quantitative determinations. F. J. M.

4839. **Chromatographic separation of phenol and cresol isomers. I.** J. Młodecka (Dept. of Physico-Chem. Methods of Analysis, Inst. of Phys. Chem., Polish Acad. of Sci., Warsaw). *Chem. Anal., Warsaw*, 1959, **4** (1–2), 157–160.—Good results in the separation of phenol and cresol isomers were obtained on Whatman papers No. 1 and 4, and on No. 4 impregnated with phosphate buffer (pH 8), with *cyclo*hexane - $CHCl_3$ - ethanol (9:1:0·6) and benzene - *cyclo*hexane - methanol (2:24:0·25) as solvents and sulphanilic acid to reveal the spots. The components separated in the following order —*o*-cresol, *p*-cresol, *m*-cresol and phenol, giving yellow - brown, purple, orange and yellow spots, respectively; only *p*- and *m*-cresols overlapped. The time required for the analysis on Whatman No. 1 paper is 2 hr., and on the buffered Whatman No. 4 is 45 min. W. B. Miaskowski

4840. **Colorimetric determination of *p*-cresol.** J. Młodecka (Anal. Dept., Inst. of Gen. Chem., Warsaw). *Chem. Anal., Warsaw*, 1959, **4** (1–2), 45–52.—The method is based on the formation of a reddish compound by the reaction of *p*-cresol with 1-nitroso-2-naphthol and $HNO_3$ in glacial acetic acid with subsequent dilution with water. The absorption is measured after 20 min. by means of a Visomat absorptiometer with green filters, a yellow soln. of the reagent being used as reference. The absorption reaches a maximum at 500 m$\mu$, and the method is suitable for concn. of 20 to 500 $\mu$g of *p*-cresol per 50 ml. Neither *m*- or *o*-cresol nor phenol interferes. For the visual comparison of the sample soln. with prepared standards the excess of the reagent can be removed after 20 min. by shaking twice with $CHCl_3$. W. B. Miaskowski

4841. **New sensitive test for quinones.** V. Anger (Lab. Dr. Anger, Vienna 18). *Mikrochim. Acta*, 1959, (3), 386–388.—Diphenylbenzidine in 75% $H_2SO_4$ reacts with *o*-quinones and *p*-benzoquinone to give a blue colour, and forms the basis of a spot-test for microgram amounts of these compounds. D. F. Phillips

4842. **Determination of crotonaldehyde and acetaldehyde in technical crotonaldehyde.** Z. Bellen and N. Bellen (Anal. Dept., Inst. of Gen. Chem., Warsaw). *Chem. Anal., Warsaw*, 1959, **4** (1–2), 19–23.—The method described enables both aldehydes to be determined simultaneously. Crotonaldehyde is determined by bromination with a soln. of $KBrO_3$ and KBr in acid medium, the excess of bromine being measured iodimetrically. For the determination of acetaldehyde, both aldehydes are condensed with $NaHSO_3$, and the acetaldehyde liberated by distillation of the product in the presence of $NaHCO_3$ is passed into a known quantity of neutralised hydroxyammonium chloride soln.; the resulting HCl is titrated with a standard soln. of NaOH. The methods are simple, rapid and sufficiently accurate for industrial purposes. Details of an apparatus for the distillation of acetaldehyde are given. W. B. MIASKOWSKI

4843. **Chromatographic analysis of mixtures of benzene polycarboxylic acids.** J.-E. Germain, J. Montreuil and P. Koukos (Centre de Carbochimie, Fac des Sci., Lille, France). *Bull. Soc. Chim. France*, 1959, **26** (1), 115–120.—The benzene polycarboxylic acids obtained by oxidising coal are separated by paper chromatography on Whatman No. 1 paper by the descending technique. The solvent system *iso*propyl alcohol - formic acid - aq. phenol (950 g of phenol in 100 ml of water) (1:2:17) separates the acids into groups of isomers. The system ethanol - aq. $NH_3$ (*d* 0·925) (7:3) separates benzoic and phthalic acids from the mixture of *iso*- and tere-phthalic acids. The system ethanol - conc. aq. $NH_3$ (1:1) separates tri- and higher poly-carboxylic acids (except benzene-1:2:3:4-tetra- and 1:2:4:5-tetra-carboxylic acids. The system butanol - acetic acid - water (4:1:5) separates tri- and higher poly-carboxylic acids (except -1:2:3-tri- from -1:2:4-tri- and -1:2:3:5-tetra- from 1:2:4:5-tetra-carboxylic acid). A complete separation of tricarboxylic and higher acids therefore can be made by two-dimensional chromatography. The spots, detected as dark spots against the blue fluorescence of the paper under u.v. light, can be cut out and extracted with 0·01 *N* NaOH and the quantity determined by u.v. absorption. The u.v. spectra of the acids in alkaline soln. are given. The synthesis of the pure acids is outlined. E. J. H. BIRCH

4844. **Chromato-polarographic studies. XIII. Analysis of mixtures of aliphatic nitro compounds.** W. Kemula and D. Sybilska (Dept. of Physico-Chem. Anal. Methods, Inst. of Phys. Chem., Polish Acad. of Sci, Warsaw). *Chem. Anal., Warsaw*, 1959, **4** (1–2), 123–134.—The chromato-polarographic method for separation of the homologous nitroalkanes is based on reversed-phase partition chromatography, with either rubber or cellulose acetate as a carrier for the liquid stationary phase. The use of cellulose acetate involves not only partition, but also adsorption on the carrier. The method covers the quant. and qual. analysis of a mixture consisting of the first six nitro derivatives of the methane series, and their separation can be carried out in the presence of 1:2-dinitroethane and 1:3-dinitropropane. The same technique can be used for the separation of higher homologues of this series. Details are given of quant. determinations by both elution and frontal methods, together with examples of the results, with emphasis on the elution procedure. The error is $\gtrsim 5\%$. The frontal method has proved accurate only in the separation of the first three or four components of the series.

W. B. MIASKOWSKI

4845. **Chromato-polarographic analysis of nitroaniline mixtures. I. Choice of the system of solvents.** H. Buchowski and W. Pawłowski (Dept. of Inorg. Chem., Warsaw Univ.). *Chem. Anal., Warsaw*, 1959, **4** (1–2), 135–143.—The difficulty in separating *m*- and *p*-nitroaniline lies in their similar ionisation constants and partition coefficients when a water - toluene solvent system is employed. The best conditions are obtained when soln. of strong acids are used as eluents. The substitution of a mixture of $CHCl_3$ and acetone for toluene increases the partition coefficients, and complete separation of *m*- and *p*-nitroaniline can be obtained on a column 4 cm high.

**II. Quantitative determination.** H. Buchowski and W. Pawłowski. *Ibid.*, 1959, **4** (1–2), 145–149.—The frontal method is used, with a 4-cm column packed with 100 mg of rubber. The aq. phase of a mixture of 1000 g of 3% aq. $H_2SO_4$, 166·5 g of acetone and 88·3 g of $CHCl_3$ is used as eluent and the $CHCl_3$ phase for swelling the rubber. All three isomeric nitroanilines can be determined directly from a chromato-polarogram if 20 ml of eluate is collected. The analysis can be accomplished much more rapidly if only the *m*- and *p*-nitroanilines are determined from an initial 7 to 8 ml of eluate, and the *o*-isomer obtained by difference from the total amount of nitroanilines determined polarographically. In order to obtain reproducible results it is necessary to plot calibration curves and carry out all analyses under strictly standard conditions. The time required for complete analysis is $<1$ hr., and the mean error is $\gtrsim 1\%$.

W. B. MIASKOWSKI

4846. **Fluorimetric micro-determination of tetraphenylboron.** Anil K. Mukherji and Bharat R. Sant (Coates Chem. Lab., Louisiana State Univ., Baton Rouge, U.S.A.). *Mikrochim. Acta*, 1959, (3), 370–371 (in English).—Preliminary experiments indicate that the sparingly soluble yellowish-white compound $(C_6H_5)_4B(C_9H_7ON)_2$ formed by the interaction of 8-hydroxyquinoline (**I**) and Na tetraphenylboron (**II**) (*cf.* Crane, *Anal. Chem.*, 1956, **28**, 1794) exhibits a characteristic green fluorescence under u.v. light which may be used for the micro-identification of $B(C_6H_5)_4^-$. *Procedure*—Place single drops of reagent (2% of **I** in glacial acetic acid), glacial acetic acid and test soln. on a filter-paper and dry carefully. Expose to u.v. light. Alternatively, instead of adding acetic acid separately to the paper, use a soln. of **II** acidified with acetic acid. To mask the ions of Be, Mg, Ca, $Zr^{IV}$, Al, Zn and Cd, which also produce fluorescence with **I**, add NaF. The limit of detection is 1 μg of **II**. D. F. PHILLIPS

4847. **Titrimetric determination of tetraphenylboron by thallium.** Bharat R. Sant and Anil K. Mukherji (Coates Chem Lab., Louisiana State Univ., Baton Rouge, U.S.A.). *Talanta*, 1959, **2** (2), 154–155.—Sodium tetraphenylboron (**I**) soln. is treated with a known excess of standard $TlNO_3$ soln. and set aside for 4 to 6 hr. The ppt. is then filtered off on a Whatman No. 42 paper, washed 8 to 10 times with about 10 ml of water, and the Tl in the filtrate titrated with standard $KIO_3$ soln. in 3 *N* to 4 *N* HCl to the ICl end-point, with $CHCl_3$ as indicator. The difference between the blank and assay titres gives the amount of **I** (1 ml of *M* $KIO_3$ soln. ≡ 0·68447 g). The relative

accuracy is ≃ 1% for amounts of **I** from 0·03 to 0·17 g. Soln. of **I** are unchanged after storage in a refrigerator for 7 days, but when stored in daylight at 30° a decrease in concn. of **I** occurs after 48 hr. R. E. ESSERY

4848. **The longest wavelength band in the electronic spectra of polycyclic aromatic hydrocarbons for analytical use.** C. Karr, jun. (Low-Temp. Tar Lab., Bureau of Mines, U.S. Dept. of the Interior, Morgantown, W. Va.). *Appl. Spectroscopy*, 1959, **13** (1), 15–25; (2), 40–45.—A table is presented listing 408 polycyclic aromatic hydrocarbons, with 3 or more aromatic rings, according to increasing values in mμ of the longest wavelength absorption band. A procedure is recommended for using this table in the analysis of samples, such as those obtained in fractionation by elution chromatography. K. A. PROCTOR

4849. **New colour tests for the larger polynuclear aromatic hydrocarbons.** E. Sawicki and R. Barry (R. A. Taft San. Engng Center, U.S. Dept. of Health, Education and Welfare, Cincinnati, Ohio). *Talanta*, 1959, **2** (2), 128–134.—Colour tests are described for polynuclear aromatic hydrocarbons of interest in the study of air pollution by carcinogens. The reagents are prepared in a specified manner with $PCl_5$ and furfuraldehyde, 2-thenaldehyde, 4-dimethylamino-3-nitrobenzaldehyde (**I**), 9-anthraldehyde (**II**) and indol-3-ylacetaldehyde. To 1 ml of test soln. are added 1 ml of reagent, 0·5 ml of $POCl_3$ and trifluoroacetic acid to a vol. of 10 ml, shaking after each addition, the spectrum being then determined against a solvent - reagent blank. Wavelength maxima and sensitivities are given for the colours given by these reagents with a number of aromatic hydrocarbons. Of the reagents studied, **II** gave intense bands in the region 800 to 960 mμ; **I** also reacted with the more basic polynuclear hydrocarbons, but gave negative results with a number of simple aromatic hydrocarbons which react with piperonylidene chloride. **I** reacts readily in most cases with the benzene extract of air-particulate samples, and is ideal for the analysis of *peri*-condensed aromatic hydrocarbons. Trifluoroacetic acid can be used in place of $PCl_5$ in preparing the reagent, but no advantage is gained thereby. R. E. ESSERY

4850. **Ultra-violet absorption spectra of 8-hydroxyquinoline and its copper chelate.** Kumar Krishna Chatterjee (Univ. Coll. of Sci., Calcutta, India). *Anal. Chim. Acta*, 1959, **20** (3), 232–235.—**I** 95% ethanol soln. 8-hydroxyquinoline shows absorption maxima at 242 mμ and 310 mμ, but in ethanolic 0·1 *N* KOH the band at 242 mμ shifts to 256 mμ, whilst in ethanolic 0·1 *N* $HClO_4$ the free ligand shows absorption maxima at 255, 310, 320 and 370 mμ. The Cu oxinate in ethanol soln. shows two maxima at 258 and 395 mμ, the 310 mμ band of the ligand having shifted to 395 mμ. From these observations a probable structure for the Cu oxinate molecule is suggested. W. J. BAKER

4851. **Separation and identification of pteridines by paper chromatography.** H. Kwietny and F. Bergmann (Dept. of Pharmacol., Hebrew Univ., Hadassah Med. Sch., Jerusalem, Israel). *J. Chromatography*, 1959, **2** (2), 162–172.—The pteridines were separated by descending chromatography on Whatman No. 1 paper. Several solvent systems were examined of which the most useful was *iso*propyl alcohol - dimethylformamide - 25% aq. $NH_3$ (13:5:2), but no single solvent could be used to separate all the pteridines studied. The separated compounds were detected with u.v. light and could be determined by u.v. spectrophotometry after extraction from the paper with phosphate buffer (pH 8). The recoveries were in the range 50 to 90%. The dependence of $R_F$ value on the composition of the solvent and the structure of the pteridines is discussed. W. T. CARTER

4852. **Determination of 5-acetamido-1:3:4-thiadiazole-2-sulphonyl chloride in the technical product.** N. Bellen and M. Szelągowska (Anal. Lab., Inst. of Gen. Chem., Pharmaceut. Inst., Warsaw). *Chem. Anal., Warsaw*, 1959, **4** (1–2), 9–11.—The sum of chloride ion and chlorine combined as sulphochloride in a sample hydrolysed by the addition of $HNO_3$ (1:1) in the presence of diethyl ether is determined potentiometrically by titration with standard $AgNO_3$ soln. The free $Cl^-$ are then determined separately by extracting the sample with $H_2O$ in the presence of diethyl ether, and titrating the acidified soln. with 0·1 *N* $AgNO_3$ as described above. W. B. MIASKOWSKI

4853. **Determination of arsenates in solutions of sodium methylarsonate and dimethylarsinate.** D. Malysz (Inst. of Drugs, Warsaw). *Chem. Anal., Warsaw*, 1959, **4** (1–2), 73–81.—Paper chromatography is employed to separate the components, and the determination of the stage of decomposition is carried out colorimetrically. Arsenates are eluted after separation, and determined in the form of arsenomolybdenum blue. Methylarsonate and dimethylarsinate interfere to a small extent, but the method is suitable for the determination of the products of decomposition to within 10% and is sufficiently accurate for pharmaceutical purposes. W. B. MIASKOWSKI

4854. **Gas-chromatographic determination of fuel dilution in lubricating oils.** R. S. Porter and J. F. Johnson (California Res. Corp., Richmond, U.S.A.). *Anal. Chem.*, 1959, **31** (5), 866–869.—A gas chromatograph is fitted with an inlet system consisting of passages in a block heated to 315°. When the sample, containing dodecane as an internal standard, is injected the volatile fractions are flashed off and swept by the carrier stream (He) through a short column kept at 175° (which traps entrained oil) into the analysing column. This method is more precise and more sensitive than the ASTM method, and samples as small as 0·25 ml can be used. G. BURGER

4855. **Gas-chromatographic determination of dissolved oxygen in lubricating oil.** P. G. Elsey (Ethyl Corp., Detroit, Mich., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 869–870.—An inlet system is described which consists of a removable U-tube fitted with two sintered glass discs and an inlet port midway between them. Dissolved gases are removed from the sample contained in this tube by the carrier gas (He) and pass into a column packed with Linde molecular sieve type 5A which separates the components. The limit of detection for O is 0·01% by vol. The standard deviation is 2·2% of the mean. The analysis time is 10 min. and the only known interference is from A, which has the same retention time as O. G. BURGER

4856. **Hydrocarbon compound-type analysis of automobile exhaust gases by mass spectrometry.** D. M. Coulson (Stanford Res. Inst., Menlo Park, Calif., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 906–

910.—Mono-olefins cannot be distinguished from cycloparaffins by their mass spectra. Separation can be achieved by passing an aliquot of the sample through a column of $Hg(ClO_4)_2$ and $HClO_4$ supported on fire-brick. With a carrier-gas flow of 110 ml per min. at 100°, olefins are quant. absorbed. The mass spectra of treated and untreated aliquots are compared. The interpretation of the spectra is discussed. G. BURGER

4857. **Investigations on *Monarda fistulosa* L. III. Colorimetric determination of thymoquinone.** E. Balcarówna and B. Borkowski (Zakład Botan. Stosowanej i Aklimatyzacji). *Biul. Inst. Roślin Leczniczych*, 1959, **5** (1), 21–26.—Earlier methods of analysis of the essential oil of this plant, containing carvacrol, thymoquinone (**I**) and thymoquinol (**II**), permitted the determination of phenols only, and consequently a new method for the determination of **I** was developed. It is based on the reaction with ethyl cyanoacetate in the presence of ethanol and conc. aq. $NH_3$. The sapphire-blue colour thus produced is stable for 1 hr. and shows a maximum absorption at 610 mμ with the use of filter S61. The extinction curve is a straight line for concn. from 0·06 to 0·2%. Although the colour reaction with ethyl cyanoacetate had been considered specific for quinones, it was found that **II** produced an identical colour under the same conditions, but this compound is unstable (being oxidised to **I**) and renders the method inapplicable to the direct determination of **I**, so that **II** must be removed by fractionation. The error is ≮5%. W. B. MIASKOWSKI

4858. **Standard methods for testing filter-paper. Introduction of the tentative standard DIN 53136: Determination of ash.** C. Bräutigam. *ChemikerZtg*, 1959, **83** (5), 158–160.—The complete text of "DIN 53136: Determination of ash" is quoted. The results of a preliminary critical evaluation of various tests for the measurement of other important properties of filter-paper which it is proposed to standardise are described. It is suggested that a modification of the method described in the U.S.A. Specification UU–P–236 for the determination of filtration rate is the most suitable for standardisation purposes, and that wet strength can be satisfactorily measured with the Herzberg apparatus or a simplified modification thereof. Separation ability can be determined by observing the retention of various ppt. [*e.g.*, $Fe(OH)_3$, $PbSO_4$ (pptd. at 80°), $BaSO_4$ (pptd. cold), and Ca oxalate] according to the quality of the paper under test. Acid- and alkali-resistance should be determined with HCl or KOH at 20° for 10 min., the concn. of the soln. depending on the quality of the paper. S. M. MARSH

4859. **Determination of lignin, cellulose and pectin materials in flax and hemp fibres.** C. Săndulescu and I. Raiu (Inst. Agron. Res.). *Acad. R.P.R., Stud. Cercet. Chim.*, 1959, **6** (3), 489–499.—*Lignin*—The method used is that of Ritter *et al.*, modified by Hölder, and further modified by the authors. The material is extracted in a Soxhlet apparatus with ethanol for 4 hr., washed with ethanol, extracted for 3 hr. with water on a water bath under reflux, washed with boiling water and ethanol and air-dried. About 1 g of extract is treated slowly with 15 ml of $H_2SO_4$ (72%) at 12° to 15° with continuous agitation. After 2 hr. the contents are diluted with water to 3% acid concn., then boiled for 4 hr. on a sand bath under reflux. The ppt. is filtered off, washed with water and dried at 105°. *Cellulose*—The method used is based on that of Kürschner and Hoffer modified by Ermakov and Arasmovici. The sample (≃1 g) is boiled under reflux for exactly 1 hr. with a mixture of 5 ml of conc. $HNO_3$ and 20 ml of 96% ethanol. The liquid is decanted off and the residue boiled again under the same conditions for 30 min., and the liquid again decanted. The residue is washed with ethanol by decantation and boiled for 30 min. in 25 ml of NaOH (1·25%) in a brine bath (25% NaCl) and filtered. The ppt. is washed with boiling water, ethanol and ether, and dried for 2 hr. at 105°. *Pectin materials*—The method used is based on the Nanji and Norman procedure. The sample (≃1 to 1·5 g so that the final ppt. is between 0·03 and 0·05 g) is extracted with 200 ml of ammonium oxalate soln. (0·5%) for 24 hr. in a thermostat at 85°, filtered hot and diluted to 250 ml with ammonium oxalate soln. A portion (100 ml) is evaporated to 20 to 25 ml, the pectin is pptd. with 90 ml of 96% ethanol (acidified with HCl), so that the final alcohol concn. is ≃70%, and filtered. The ppt. is washed with ethanol to eliminate oxalate and dissolved in very dil. boiling aq. $NH_3$. The soln. is treated with 0·1 *N* NaOH to obtain pectic acid, and after several hours 50 ml of *N* acetic acid plus 50 ml of *M* $CaCl_2$ is added and the mixture is set aside overnight. The Ca pectate is coagulated by heating, filtered off while hot, washed with hot water, evaporated on a water bath and dried at 105°. H. SHER

4860. **Qualitative chromatographic identification of mildew inhibitors on military fabrics.** T. D. Miles and A. C. Delasanta (U.S. Army Quartermaster Res. and Engng Center, Natick, Mass.). *Amer. Dyest. Rep.*, 1959, **48** (7), 31–32.—The fabric (5 g) is boiled with 200 ml of $CCl_4$ until the vol. is reduced to 100 ml. The soln. is chromatographed on a circular paper, butanol - water - conc. HCl (8:1:1) being used to separate Cu 8-hydroxyquinolinate, Cu naphthenate, di-(5-chloro-2-hydroxyphenyl)methane and the zinc salt of dithiocarbamic acid, and 2·5% aq. NaOH soln. - ethanol (17:3) for salicylanilide. For the colour development, the paper is exposed to $NH_3$ fumes, and examined under u.v. light. It is then cut in half, one half being wetted with a 0·01% soln. of dithizone in $CCl_4$ and then dried, the other half being wetted with a 2% soln. of 4-aminophenazone in 0·025% $Na_2CO_3$ soln., then with 8% aq. $K_3Fe(CN)_6$ soln., and then exposed to $NH_3$ fumes; $R_F$ values and colours are tabulated.

S.C.I. ABSTR.

4861. **Determination by means of the infra-red spectrometer IKS-12 of products obtained in caprolactam manufacture.** L. G. Zelenskaya, A. V. Iogansen and G. A. Kurkchi (State Sci. Res. and Devel. Inst. of the Nitrate Ind. and Products of Org. Synthesis). *Zavod. Lab.*, 1959, **25** (3), 299–300.—The determination of the hydrogenation and nitration products of benzene and of various gases are referred to. G. S. SMITH

4862. **Mass-spectrometric determination of the composition of raw materials and intermediates in the production of caprolactam.** V. Čermák and V. Hanuš (Inst. Phys. Chem., Acad. Sci., Prague). *Chem. Průmysl*, 1959, **9** (5), 235–237.—It is claimed that by means of a mass spectrometer it is possible to determine the content of homologues and impurities of higher mol. wt. in concn. ≃ 0·01%

(w/v). The accuracy of the analysis depends mainly on preliminary treatments by means of which the influence of the adsorptive properties of the test samples is removed or decreased. With the instrument used the following determinations can be carried out: *o*-cresol in phenol, phenol in *cyclo*hexanol or *cyclo*hexanone, *cyclo*hexanol in *cyclo*hexanone, methyl*cyclo*hexanone in *cyclo*hexanol or *cyclo*hexanone, methyl*cyclo*hexanol in *cyclo*hexanol or *cyclo*hexanone, methylcaprolactam in caprolactam or *cyclo*hexylidene*cyclo*hexanone. The highest accuracy was reached in determining methyl*cyclo*hexanone in *cyclo*hexanone (1 to 2% rel.) and the lowest in determining *o*-cresol in *cyclo*hexanol (10 to 20% rel.). The ionic source of the mass spectrometer is connected by a capillary tube to a 3-litre reservoir into the neck of which are fused two tubes, one of which is connected to a mercury diffusion pump through a valve packed with metallic indium and the other contains a sintered-glass disc covered with mercury. The sample to be analysed is sucked into the exhausted reservoir through a capillary tube in contact with the sintered glass disc below the surface of the mercury. J. ZÝKA

4863. **Determination of maleic acid in its copolymers with vinyl chloride and vinyl acetate.** P. Maltese, T. Di Gioacchino and E. Garzuglia (Inst. Ricerche "Polymer", Terni, Italy). *Chim. e Ind.*, 1959, **41** (3), 218–221.—The polymer is dissolved in pyridine in the presence of small amounts of water, and maleic acid is titrated with 0·1 *N* Na methoxide in methanol - benzene, or with NaOH in *iso*propyl alcohol, the end-point being detected with thymol blue or phenolphthalein, or potentiometrically. C. A. FINCH

4864. **Chlorine in bleached shellac.** O. Tweet, W. K. Miller and R. H. Simon (S. C. Johnson & Sons Inc., Racine, Wis., U.S.A.). *Soap, N.Y.*, 1959, **35** (3), 95–99.—Methods for the determination of total Cl and Cl as chloride are outlined and discussed. Chloride is often incompletely extracted by shaking the ground sample with water, as the degree of extraction depends on the size of the particles. The following procedures are recommended. *Chloride*—The sample (1 g) is dissolved in *n*-butanol and the $Cl^-$ are extracted with water. The aq. extract is strongly acidified with $HNO_3$, and the $Cl^-$ are titrated potentiometrically with 0·02 *N* $AgNO_3$. *Total chlorine*—(*i*) The sample (1 g) is dissolved in *iso*propyl alcohol, and reduced by heating under reflux with metallic sodium (2·5 g). The cooled liquid is diluted with water, acidified with $HNO_3$, and an excess of 0·1 *N* $AgNO_3$ is added, and back-titrated with 0·1 *N* KSCN. (*ii*) The sample (0·3 g) is decomposed in a Parr bomb, the melt is dissolved in water, acidified with $HNO_3$, and the $Cl^-$ are titrated potentiometrically as described above. The Parr bomb method is probably slightly more accurate, but the reduction method is more rapid, and needs no special equipment. S.C.I. ABSTR.

4865. **Methods of analysis for tall-oil products.** R. Herrlinger (Arizona Chem. Co., Panama City, Fla., U.S.A.). *J. Amer. Oil Chem. Soc.*, 1959, **36** (3), 119–124.—A review is presented of the principal U.S. standard methods (mainly A.S.T.M.) for the chemical and physical analysis of tall-oil products. G. R. WHALLEY

4866. **EDTA titration of copper in copper linoleate.** C. A. Lucchesi, J. A. Stearns and C. F. Hirn (Anal. Res. Dept., Sherwin-Williams Co., Chicago, Ill., U.S.A.). *Chemist Analyst*, 1959, **48** (1), 9–10.—Treat the sample (0·15 g) with 10 ml of $HNO_3$ (1:3) and heat to boiling for 10 to 30 min., till all the Cu is in solution. Filter into a 250-ml beaker and wash the filter well with hot water, not allowing it to run dry. Add aq. $NH_3$ (1:3) to the filtrate till a blue or green colour appears, then continue the addition dropwise to pH 7 (indicator paper). The mixture should then measure about 125 ml. Add 1 ml of glacial acetic acid and 6 drops of 0·1% 1-(2-pyridylazo)-2-naphthol soln. as indicator and titrate with 0·01 *M* EDTA (disodium salt) to a yellow - green colour. To facilitate recognition of the end-point, use a comparison soln. of 6 drops of indicator soln. in 125 ml of acidified water. Duplicate determinations occupy 1 hr., and results show good replication and close agreement with results by the electro-deposition procedure. R. E. ESSERY

4867. **Polarographic determination of dibutyl phthalate in propellent compositions containing nitroglycerin.** A. F. Williams and D. Kenyon (Res. Dept., I.C.I. Ltd., Nobel Div., Stevenston, Scotland). *Talanta*, 1959, **2** (1), 79–87.—It is not possible to determine dibutyl phthalate in ether extracts of explosives because of interference from nitroglycerin, but the determination can be carried out with a cathode ray polarograph. Nitroglycerin enhances the height of the dibutyl phthalate peak, but this effect becomes constant at approx. 80 $\mu$g of nitroglycerin per ml, above which a blank value can be deducted. *Procedure*—Extract the sample (1 g) with diethyl ether for 6 hr. Evaporate the extract to dryness and dilute to 100 ml with methanol. Dilute 10 ml of this soln. to 100 ml with methanol and take a 10-ml aliquot. Add tetramethylammonium iodide soln. (0·2 *M*) (10 ml), remove O by passing N for 10 min. and polarograph, measuring the peak height at $-1{\cdot}52$ V (mercury pool). Carry out a blank on a soln. of nitroglycerin containing $\leqslant 80$ $\mu$g per ml. Results are in good agreement with the dibutyl phthalate content found by difference when a complete analysis procedure is used. W. T. CARTER

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*See also Abstracts*—**4658**, Schiff's reagent of calibrated sensitivity. **4722**, Determination of N. **4724**, Determination of aniline in hydrazine. **4726**, Phosphorus in coal and coke. **4899**, Determination of quinolinic acid. **4962**, **4963**, **4964**, **4965**, **4966**, Dyes in foods. **4981**, Detection of carboxylic acids and aldehydes in air-borne particles. **5017**, Determination of $H_2O$ in textiles. **5029**, Use of $Ag^{131}I$ in chromatography of organic acids. **5033**, Gas chromatography of organic compounds.

## 4.—BIOCHEMISTRY
## INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

### Biological fluids, animal and vegetable tissues

4868. **Analysis of gas in biological fluids by gas chromatography.** L. H. Ramsey (Dept. of Med., Vanderbilt Univ., Nashville, Tenn., U.S.A.). *Science*, 1959, **129**, 900–901.—The permanent gases in the sample fluid, *e.g.*, plasma (1 ml), are extracted

in a Van Slyke volumetric vacuum extraction chamber, and injected into the carrier stream (He) of a gas chromatograph (Beckman GC-2). The method is illustrated by the determination of oxygen tension in plasma.

H. F. W. KIRKPATRICK

4869. **Radiometric determination of sodium in blood serum.** J. Dobrowolski and N. Wyszyński (Med. Acad. Szczecin). *Chem. Anal., Warsaw*, 1959, **4** (1–2), 207–212.—The method consists in measuring the intensity of the radiation produced by the uranyl - sodium complex by means of a Geiger - Müller counter. The ppt. from this determination was weighed to compare the results obtained by radiometric and gravimetric methods, and it was found that the accuracy of both is of the same order. The error of determination is $\gtrsim 4\%$.

W. B. MIASKOWSKI

4870. **Rapid micro-method for determining serum calcium.** I. M. Bett and G. P. Fraser (Dept. of Clin. Chem., Univ. of Aberdeen, Scotland). *Clin. Chim. Acta*, 1959, **4** (3), 346–356.—The proposed method consists in titrating the Ca in serum (0·1 ml) directly with EDTA soln. by using a micro-syringe, with calcein as indicator. The end-point is determined by observing the disappearance of fluorescence in u.v. light. Suitable apparatus is described.

H. F. W. KIRKPATRICK

4871. **Ultra-micro determination of serum calcium.** P. Cartier and J. Clement-Métral (Fac. de Méd., Paris, France). *Clin. Chim. Acta*, 1959, **4** (3), 357–363.—The method is similar to that of Bett and Fraser (*Anal. Abstr.*, 1959, **6**, 4870), the disappearance of the fluorescence during the titration being automatically recorded.

H. F. W. KIRKPATRICK

4872. **Determination of copper and zinc in biological material by activation analysis.** H. J. M. Bowen (Technol. Irradiation Group, Isotope Div., Wantage Radiation Lab., Grove, Berks., England). *Intern. J. Appl. Radiation and Isotopes*, 1959, **4** (3–4), 214–220.—Tomato seeds and blood were irradiated with standards containing $\simeq 0{\cdot}1$ μg of Cu and 20 μg of Zn in a thermal neutron flux of $10^{12}$ *n* per sq. cm per sec. for 12 hr. The subsequent separation procedures for the Cu and Zn are described; they take about 2 hr. and 2·5 hr., respectively. It is estimated that $4 \times 10^{-10}$ g of activated Cu or $5 \times 10^{-8}$ g of activated Zn would produce a count-rate equal to the background count-rate of an end-window counter.

G. J. HUNTER

4873. **Micro-determination of zinc in blood and other tissues by neutron activation analysis.** T. E. Banks, R. Tupper, E. M. A. White and A. Wormall (Dept. of Biochem. and Physics, Med. Coll., St. Bartholomew's Hosp., London). *Intern. J. Appl. Radiation and Isotopes*, 1959, **4** (3–4), 221–226.—The sample was dried and then irradiated for 28 hr. in BEPO with standards containing 2 μg and 4 μg of Zn and one of 20 to 30 mg of $ZnSO_4$ that was used to facilitate calibration of the counting equipment. The radiochemical separation of the Zn and the subsequent γ-counting of the 14-hr. $^{69m}$Zn are described. The mean recovery of Zn (0·78 to 2·0 μg) added to seven samples of blood (0·15 to 0·28 g) was 101%. The content of Zn of mouse liver was found to be $27{\cdot}0 \pm 0{\cdot}6$ μg in 5 determinations; a chemical method gave a content of 28·4 μg.

G. J. HUNTER

4874. **Determination of traces of mercury in biological material by catalytic action of mercuric ions. Micro-electrolysis of mercury.** D. Pavlović and S. Ašperger (Inst. of Inorg., Anal. and Phys. Chem., Fac. of Pharm., Univ. of Zagreb, Yugoslavia). *Anal. Chem.*, 1959, **31** (5), 939–942.—Ash the sample of blood (5 ml) or urine (25 ml) in the presence of $HNO_3$, sublime the mercury in a stream of Br vapour and absorb it in bromine water. Electrolyse the soln. between platinum electrodes, re-dissolve the deposited mercury in bromine water and expel the excess of Br by evaporation. Alternatively, use a gold cathode and dissolve the deposit in conc. $HNO_3$. Determine the concn. of $Hg^{2+}$ in the purified soln. by the catalytic effect on the reaction of $K_4Fe(CN)_6$ with nitrosobenzene at pH 4·1 to give a violet-coloured product (*cf.* Ašperger and Murati, *Anal. Abstr.*, 1954, **1**, 1789). Quantities of 0·002 to 0·050 μmole of Hg can be determined with a coeff. of variation of $\simeq \pm 20\%$.

A. R. ROGERS

4875. **Determination of thallium in urine and air.** E. E. Campbell, M. F. Milligan and J. A. Lindsey (Los Alamos Sci. Lab., N. Mex.). *Amer. Ind. Hyg. Ass. Quart.*, 1959, **20**, 23–25.—Recoveries of Tl average $96 \pm 6\%$. Procedures are given for the preliminary preparation of samples, for the preparation of the standard curve, for the oxidation of thallous ion to thallic ion, and for the extraction and measurement of the Tl - methyl violet complex.

NUCL. SCI. ABSTR.

4876. **Polarographic determination of lead in urine in the presence of EDTA with use of an ion exchanger to remove interfering substances.** J. Chmielowski and Z. Myslak (Clin. Dept., Med. Inst. in Mining and Metall. Ind., Zabrze). *Chem. Anal., Warsaw*, 1959, **4** (1–2), 233–239.—A polarographic method for determining Pb in the urine of patients suffering from plumbism and treated with salts of EDTA consists in acidifying 3 ml of the sample (to pH < 1) with 2 ml of 8% HCl, passing the soln. through a column (15 cm) of Wofatit P (H form) to adsorb interfering substances, bubbling $CO_2$ through the percolate for 2 min., suppressing frothing with a trace of 2-ethylhexanol, and then examining the soln. polarographically. Concn. of Pb >30 μg per 100 ml can be determined. With concn. >50 μg per 100 ml the error is $\simeq \pm 6{\cdot}5\%$.

W. B. MIASKOWKI

4877. **Spectrophotometric determination of chromium in human plasma and red cells.** D. O. Miller and J. H. Yoe (Dept. of Chem., Univ. of Virginia, Charlottesville, U.S.A.). *Clin. Chim. Acta*, 1959, **4** (3), 378–383.—The method is based on the red - violet complex formed by the reaction of dichromate with diphenylcarbazide. The concn. of Cr found in normal human plasma ranged from 0·017 to 0·052 p.p.m., and in red cells from 0·014 to 0·038 p.p.m.

H. F. W. KIRKPATRICK

4878. **Estimation of iodine in urine.** G. Widström and K. Claeson (Clin. Lab. Centrallasarettet, Danderyd, Sweden). *Acta Chem. Scand.*, 1959, **13** (3), 606–607 (in English).—Calcium causes low results owing to loss of $CaI_2$ during incineration. This can be avoided by a preliminary treatment of the urine with ammonium oxalate to remove Ca. The sample is then incinerated with Zn acetate and $K_2CO_3$ for 3 hr. at 600°. The residue is dissolved in *N* HCl and the iodine determined colorimetrically by the arsenite - ammonium ceric sul-

phate method. The average recovery of iodine is 96% compared with 83% when $Na_2CO_3$ is used for the incineration. W. T. CARTER

4879. **Combustion of body fluids in oxygen, and its application to the determination of iodine in fluids containing contrast media.** H. Langecker (Schering A.-G., West Berlin). *Klin. Wochschr.*, 1959, **37** (8), 471–472.—Urine or bile (0·5 ml) is absorbed on a filter-paper cone, and dried at 60° to 80°. The paper is then burnt in a flask containing oxygen, the products of the combustion being absorbed by a carbonate - nitrate soln. After oxidation of the resulting soln. with bromine, the iodate content is determined by titration with standard $Na_2S_2O_3$ soln. This method gives recoveries of 99 to 104% over a range of 6·7 to 670 mg of iodine per 100 ml. Owing to the production of peroxides, this method cannot be used for the determination of serum-protein-bound iodine by the ceric - arsenite catalytic reduction method.

D. B. PALMER

4880. **Spectrophotometric determination of NN′-diisonicotinoylhydrazine (DINH) in the presence of isoniazid and its metabolites.** B. P. Lisboa (Tuberkulose-Forschungsinst., Borstel über Bad Oldesloe). *Naturwissenschaften*, 1959, **46** (3), 109.—A soln. (5 ml, containing 25 to 500 $\mu$g) of these substances in 0·067 *M* phosphate buffer (pH 7·2) is treated with 0·5 ml of a freshly prepared 0·25% aq. soln. of trisodium pentacyanoamminoferrate (*cf.* Herington, *Analyst*, 1953, **78**, 174). After being heated in a water bath at 60° for 15 min. the soln. is cooled and the extinction is measured at **333** m$\mu$ against a blank. DINH shows a selective absorption max. at this wavelength and its concn. may be obtained from a standard curve.

H. F. W. KIRKPATRICK

4881. **Improved glucose oxidase method for determining blood, cerebrospinal fluid and urine glucose levels.** V. Marks (Inst. of Neurol., Nat. Hosp., London, England). *Clin. Chim. Acta*, 1959, **4** (3), 395–400.—The method of Middleton and Griffiths (*cf. Anal. Abstr.*, 1958, **5**, 3087) is modified by the substitution of an acetate for the phosphate buffer soln. This is prepared by mixing 3 vol. of 0·15 *M* acetic acid with 7 vol. of 0·15 *M* Na acetate and adjusting the pH to 5·0.

H. F. W. KIRKPATRICK

4882. **Experience with a glucose oxidase method for estimating glucose in blood and cerebrospinal fluid.** J. E. Middleton (St. Thomas's Hosp. Med. Sch., London, England). *Brit. Med. J.*, 1959, **i**, 824–826.—The enzyme method of Middleton and Griffiths (*cf. Anal. Abstr.*, 1958, **5**, 3087) used in parallel with an older chemical method (MacLean) showed non-glucose reducing substances to vary from 0 to 81 mg per 100 ml (mean 35) in normal and diabetic blood. Glucose tolerance can be assessed satisfactorily on capillary blood by the glucose method, but results with the older sugar method are erratic. Glucose fasting levels in normal capillary blood range from 46 to 94 mg per 100 ml (mean 69), and the normal renal threshold is approx. 160 mg per 100 ml. In normal cerebrospinal fluid, glucose concn. varies from 50 to 76 mg per 100 ml (mean 63), and non-glucose reducing substances average 19 mg per 100 ml.

H. F. W. KIRKPATRICK

4883. **The behaviour and characterisation of D-galactose in the routine examination of urine.** G. Zinner (Inst. f. Pharm. Chem. u. Lebensmittelchem., Univ., Marburg/Lahn). *Dtsch. ApothZtg.*, 1959, **99** (16), 371–373.—A review is given of the behaviour of galactose in the usual tests for sugars.

A. R. ROGERS

4884. **A sensitive and stereospecific enzymic assay for xylulose.** J. Hickman and G. Ashwell (Nat. Inst. of Arthritis and Metabol. Diseases, Bethesda, Md., U.S.A.). *J. Biol. Chem.*, 1959, **234** (4), 758–761.—D- and L-xylulose are determined alone, or when mixed, by two enzymes (triphosphopyridine nucleotide-xylitol (L-xylulose) dehydrogenase and diphosphopyridine nucleotide-xylitol (D-xylulose) dehydrogenase which are prepared from guinea-pig liver acetone powder. In the presence of the appropriate reduced pyridine nucleotide the specific dehydrogenase reduces the xylulose to xylitol, and the rate of oxidation of the reduced nucleotide is determined spectrophotometrically at 340 m$\mu$. The triphosphopyridine nucleotide-linked enzyme is specific for L-xylulose, but the other dehydrogenase reacts equally well with D-xylulose and L-erythrulose. J. N. ASHLEY

4885. **Investigation of the fucose content of serum, and of protein fractions. I. Method of determination and normal serum levels.** M. Jacubeit, P. Brünger and M. Knedel (Med. Clinic, Univ. of Munich). *Klin. Wochschr.*, 1959, **37** (8), 460–464.—Serum fucose is estimated by the method of Dische and Shettles for methylpentoses (*J. Biol. Chem.*, 1948, **175**, 595). Three aliquots of 0·05 ml to 0·10 ml of serum are required for each determination—a test sample, an "internal standard" and a serum blank. The serum is deproteinised by the addition of 5 ml of 96% ethanol, and after being set aside for 20 min. the soln. are centrifuged, and the supernatant liquid is discarded; 1 ml of 0·1 *N* NaOH is added to each tube, and to a reagent blank tube, but not to the "internal standard". This contains 0·9 ml of 0·1 *N* NaOH and 0·1 ml of a standard fucose soln. (10 mg per 100 ml). All the tubes are cooled in ice-water, and after the addition of 4·5 ml of 27·8 *N* $H_2SO_4$ the contents are well mixed and re-cooled. The tubes are then heated in a boiling-water bath for 10 min. and, after cooling under running water, 0·1 ml of a 3% aq. soln. of cysteine hydrochloride is added to each tube except that containing the serum blank, to which 0·1 ml of water is added. After a thorough shaking the colour is allowed to develop by standing the tubes in a bath of running water for 5 hr., in the dark. The soln. are then given a final mixing and all the air bubbles are removed before measuring the colours photometrically at 396 and 430 m$\mu$, with 0·5-cm cells and reading against the reagent blank. The true extinction coeff. is obtained by taking the difference of these two values. The various factors affecting the determination are discussed. Normal values for serum are 8·31 $\pm$ 2·236 mg per 100 ml, or 0·10 to 0·13% in terms of total serum protein, for the 20 subjects studied.

D. B. PALMER

4886. **Quantitative chromatography of carbohydrate constituents of glycoproteins.** J. Montreuil and N. Scheppler (Lab. de Chim. Biol., Fac. de Méd. et Pharm., Lille). *Bull. Soc. Chim. Biol.*, 1959, **41** (1), 13–27.—The amount of carbohydrate determined by hydrolysis and paper chromatography is less by 20 to 50% than that determined by direct colorimetry with orcinol on the pure mucoprotein. Studies on the kinetics of acid hydrolysis of polysaccharides both pure and in

the presence of protein, and combined as mucoprotein, show that treatment with 1 *N* HCl for 1 to 4 hr. effects complete hydrolysis of glycoprotein; $H_2SO_4$ alters the kinetics of the hydrolysis and favours the condensation of sugars with liberated amino acids. Either acid (1 *N* or 2 *N*) is suitable for the hydrolysis of pure polysaccharides which do not contain ketoses. Pentoses are particularly labile. In view of the labile character of certain types of glycosidic bonds, a preliminary systematic investigation of the hydrolysis kinetics for a particular polysaccharide or glycoprotein is recommended. A procedure for the ion-exchange purification and paper-chromatographic analysis of the hydrolysates that gives good recoveries of sugars is described. D. W. Moss

4887. **Separation and quantitative determination by paper chromatography of protein-bound carbohydrates.** R. Bourrillon and J. Michon (Lab. Biochim., Fac. de Méd., 45, rue des Saint-Pères, Paris). *Bull. Soc. Chim. Biol.*, 1959, **41** (2–3), 267–276.—A study of the conditions necessary to obtain optimum separation of protein-bound carbohydrates is presented. By using different chromatographic papers in conjunction with several neutral, acid and alkaline solvents it is shown that S. & S. 2043b acid-washed paper, with any of the following solvents, gives the best separation—*n*-butanol - pyridine - water (5:3:2), *n*-butanol - pyridine - 0·1 *N* HCl (5:3:2) (**I**), *iso*amyl alcohol - pyridine - water (4:4:2) or *iso*amyl alcohol - pyridine - 0·1 *N* HCl (4:4:2) (**II**). The chromatograms are developed by descending chromatography for 16 to 20 hr. at 22° to 23° and, after drying the papers at 100° for 5 min. or at 80° for 30 min., the marker strips are sprayed with a soln. of aniline oxalate. The areas containing the separated sugars are cut out, eluted overnight with double-distilled water at 4°, and aliquots of the resulting soln. are analysed by the methods of Elson and Morgan (*Biochem. J.*, **1933, 27, 1824**) for osamines, and of Somogyi and Nelson (*J. Biol. Chem.*, 1945, **160**, 61; 1944, **153**, 375) for hexoses and fucose. By using either **I** or **II**, fucose, rhamnose, mannose, glucose, galactose, glucosamine, galactosamine, sialic acid and glucuronic acid can be separated with recoveries of 95 to 103% at levels of 50 to 150 μg of hexoses, 25 to 100 μg of hexosamines, and 20 to 30 μg of fucose. The $R_F$ values of the various compounds are given for the systems used, and the advantages of the method, in particular the separation of glucosamine and galactosamine, are discussed.
D. B. Palmer

4888. **Methods for the isolation of glycolytic intermediates by column chromatography with ion-exchange resins. [Assay of carbohydrate phosphates.]** G. R. Bartlett (Scripps Clinic and Res. Foundation, La Jolla, Calif., U.S.A.). *J. Biol. Chem.*, 1959, **234** (3), 459–465.—To improve the assay of carbohydrate phosphates in eluates from column chromatography, modifications are described and additional information given for the anthrone, carbazole, cysteine - $H_2SO_4$ and periodate methods of determination. J. N. Ashley

4889. **Studies on materials containing uronic acid. I. An apparatus for routine semi-micro estimations of uronic acid content.** D. M. W. Anderson (Dept. of Chem., Univ., Edinburgh, Scotland). *Talanta*, 1959, **2** (1), 73–78.—A simplified apparatus is described and illustrated for use with the Lefèvre and Tollens decarboxylation reaction. The sample (sufficient to liberate 1 to 5 mg of $CO_2$) is heated under reflux with 35 ml of 19% HCl for 2·5 hr. and the $CO_2$ evolved is removed by a stream of N (15 ml per min.), absorbed in 0·05 *N* $Ba(OH)_2$ and determined by back-titration with 0·05 *N* HCl. Results are quoted for the analysis of glucuronic acid lactone, galacturonic acid monohydrate and Hakea gum. W. T. Carter

4890. **Formation of 2-oxo-3-deoxyheptonic acid in extracts of *Escherichia coli* B. I. Identification [and determination].** A. Weissbach and J. Hurwitz (Nat. Inst. of Arthritis and Metabol. Diseases, Bethesda, Md., U.S.A.). *J. Biol. Chem.*, 1959, **234** (4), 705–709.—A very sensitive and specific method is described for the detection and determination of sugar acids that contain a 2-oxo-3-deoxy grouping. It depends on the oxidation of the deoxy compound with $HIO_4$ and reaction of the product with thiobarbituric acid to give a chromogen with max. absorption at 548 mμ. Any compound which gives formylpyruvic acid when oxidised by $HIO_4$ will respond to the test.
J. N. Ashley

4891. **Colorimetric assay methods for free and phosphorylated glyceric acids.** G. R. Bartlett (Scripps Clinic and Res. Foundation, La Jolla, Calif., U.S.A.). *J. Biol. Chem.*, 1959, **234** (3), 469–471.—Spectra are given for the coloured products formed when glyceric acid, monophosphoglyceric acid and 2:3-diphosphoglyceric acid are heated with 1:3- or 2:7-dihydroxynaphthalene or chromotropic acid in $H_2SO_4$ at 100° for 30 min. Chromotropic acid is the best reagent for the assay of such compounds and the intensity of the colour at 695 mμ is proportional to the concn.
J. N. Ashley

4892. **Isolation of carotenoids, coumestrol, chlorogenic acid and antibiotics. Application of countercurrent distribution.** C. R. Thompson, A. L. Curl and E. M. Bickoff (W. Regional Res. Lab., Albany, Calif., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 838–841.—The application of the countercurrent distribution technique to biologically active materials is reviewed briefly and examples showing its uses are given. A. R. Rogers

4893. **Photometric determination of flavonoids.** B. Borkowski and S. Czyszewska. *Biul. Inst. Roślin Leczniczych*, 1958, **4** (4), 340–355.—Seven methods for the quant. determination of flavonoids have been described and compared, using rutin and robinin as standard samples. That due to Horák was the most sensitive and simple, and was found to be useful as a micro-method, its only disadvantage being a low stability of the coloured complex. *Determination of rutin*—Extract 0·25 g of dried, powdered sample (or 2·5 g of fresh sample) in a Soxhlet apparatus with methanol - pyridine (20:1) for 90 min. (for a fresh sample do not use pyridine). Dilute the extract to 25 ml and spot 100-μl aliquots on Whatman No. 4 paper together with standard spots of quercetin soln. corresponding to 1 to 5 μg of quercetin. Chromatograph by the descending technique with 60% acetic acid for 2 to 3 hr. Determine the quercetin by comparing the fluorescence with standards under u.v. light. Cut out the coloured spot due to rutin and extract for 30 min. with 5 ml of 0·5% aq. $NH_3$ soln. with frequent shaking. Add 1 ml of diazotised sulphanilic acid and shake. After 2 min. add 2 ml of *N* HCl and after 15 min. measure the extinction in a 2-cm cell with an S42 filter against a blank. W. Roubo

4894. **Separation of antibodies by starch zone electrophoresis.** P. Stelos and W. H. Taliaferro (Dept. of Microbiol., Univ. of Chicago, Ill., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 845–848.—Two haemolysins, of mol. wt. $\simeq$ 160,000 and 1,000,000, respectively, have been separated from rabbit antisera against sheep red cells by starch zone electrophoresis in a barbiturate buffer of pH 8·6 and ionic strength 0·1. The antibody recovery ranged from 70 to 90%. A. R. ROGERS

4895. **Phosphorus assay in column chromatography.** G. R. Bartlett (Scripps Clinic and Res. Foundation, La Jolla, Calif., U.S.A.). *J. Biol. Chem.*, 1959, **234** (3), 466–468.—A modification of the Fiske and Subbarow method is described. It is based on the large increase in light absorption at 830 m$\mu$ which is produced when the reaction mixture used in the determination is heated with $\simeq$ 10 *N* $H_2SO_4$ at 150° to 160°. The colour produced is stable at room temp. for at least 24 hr., and the amount of P is ascertained from a standard curve. The method (a modification for ultra-micro work is also described) has greatly increased sensitivity and reliability, and is very useful for multiple determinations of total P on eluates from chromatographic columns. J. N. ASHLEY

4896. **Colorimetric estimation of serum fatty esters.** H. L. Rosenthal, M. L. Pfluke and J. Callerami (Rochester Gen. Hosp., N.Y., U.S.A.). *Clin. Chim. Acta*, 1959, **4** (3), 329–333.—The method of Stern and Shapiro (*J. Clin. Path.*, 1953, **6**, 158) is modified and cryst. cholesteryl acetate (**I**) is used as standard. *Procedure*—To 15 ml of Bloor's reagent add 0·5 ml of serum, with shaking, bring to boiling on a steam bath, cool, and dilute to 25 ml with solvent. Prepare a stock standard soln. by dissolving 215 mg of dry **I** in Bloor's solvent and dilute 20 ml of this soln. to 100 ml with solvent to obtain the working soln. containing 0·5 $\mu$mole per ml. To 5 ml each of test filtrate, working standard and solvent (blank) add with mixing 1 ml of 2 *M* hydroxyammonium chloride and 1 ml of 3·38 *N* NaOH, and allow to stand at room temp. for 20 to 30 min. Add with mixing 1 ml of 3·8 *N* HCl and 1 ml of 10% $FeCl_3.6H_2O$ in 0·1 *N* HCl. After 10 min. read the extinctions at 520 m$\mu$. H. F. W. KIRKPATRICK

4897. **The DDT content of human fat.** H. Maier-Bode (Pharmacol. Inst., Univ., Bonn). *Angew. Chem.*, 1959, **71** (5), 188–189.—The method of Mattson *et al.* (*Anal. Chem.*, 1953, **25**, 1065) was re-examined. The Davidow column, as used in the original procedure, left some impurities in the fat which reacted similarly to DDT; by using kieselguhr - $H_2SO_4$ - $Al_2O_3$ - $Na_2CO_3$ as packing, instead of kieselguhr - $H_2SO_4$ alone, this error was eliminated. The highest value for DDT plus DDE [1;1-dichloro-2;2-di-(*p*-chlorophenyl)ethylene] found in 21 samples was 10 p.p.m. Some of the analytical results were confirmed by biological experiments. A. G. PETO

4898. **Fluorimetric method for the differential estimation of 3-O-methylated derivatives of adrenaline and noradrenaline (metanephrine and normetanephrine).** A. Bertler, A. Carlsson and E. Rosengren (Dept. of Pharmacol., Univ. of Lund, Sweden). *Clin. Chim. Acta*, 1959, **4** (3), 456–457 (in English).—The oxidation of these derivatives at pH 7·2 followed by alkaline treatment yields compounds with activation and fluorescence spectra identical with those obtained from the parent amines. Oxidation at pH 5, however, gives no fluorescence with the methylated compounds, and this can be used to differentiate these derivatives. The following procedure is proposed for the differential determination of metanephrine (**I**) and normetanephrine (**II**). Adjust the pH of the sample to $\simeq$7·2 and to 1 to 3 ml add 0·5 ml of 0·1 *M* phosphate buffer (pH 7·2), $H_2O$ to a vol. of 3·8 ml, and 0·05 ml of 0·02 *N* iodine. After 5 min. add 0·5 ml of 4·5 *N* NaOH containing 0·2% of ascorbic acid. After 5 min. add 0·6 ml of 5 *N* acetic acid and read the fluorescence in a spectrophotofluorimeter as follows—**I**, activation 420 m$\mu$, fluorescence 530 m$\mu$; and **II**, activation 395 m$\mu$, fluorescence 515 m$\mu$. H. F. W. KIRKPATRICK

4899. **3-Hydroxyanthranilic acid metabolism. VII. Mechanism of formation of quinolinic acid. [Determination of quinolinic acid.]** S. W. Moline, H. C. Walker and B. S. Schweigert (Div. of Biochem. and Nutr., Amer. Meat Inst. Foundation, Chicago, Ill., U.S.A.). *J. Biol. Chem.*, 1959, **234** (4), 880–883.—Quinolinic acid, after purification on a Dowex-1 anion-exchange column and elution with 0·1 *M* $CaCl_2$, is determined spectrophotometrically at 268 m$\mu$ using a predetermined mol. extinction coeff. of 3610. J. N. ASHLEY

4900. **Estimation of α-amino nitrogen by the method of Stanek and Pavlas.** R. Carolan. *Int. Sugar J.*, 1959, **61** (2), 44–45.—Turbidity in the soln. for colorimetry prepared according to the original method (Stanek and Pavlas, *Z. Zuckerind. Czech. Rep.*, 1935, **59**, 129) is avoided by the use of a modified reagent. Dissolve 250 g of cryst. Na acetate in about 450 ml of warm $H_2O$, and to the cooled soln. add 10 g of copper nitrate dissolved in 200 ml of $H_2O$. Add 50% acetic acid in 2-ml portions with constant stirring until the pH is between 6·1 and 6·3. Make up to 1 litre, allow to stand overnight and filter. Asparagine standards are used (Stehlík and Cerny, *Ibid.*, 1934, **59**, 284). The blue colour is measured at 650 m$\mu$ against a reagent blank. H. F. W. KIRKPATRICK

4901. **Continuous amino-acid separation on an ion-exchange resin by gradient elution with buffer solution.** H. Stegemann (Med. Forschungsanst. d. Max-Planck-Gesellsch., Silikoselabor, Göttingen, Germany). *Naturwissenschaften*, 1959, **46** (3), 110.—Dowex 50-X8, 200 to 400 mesh, prepared in OH form, is used for the column (160 cm × 9 to 10 mm), which is maintained at 40°. Citrate buffer (pH 3·30 $\pm$ 0·02) is used for elution, the eluate being collected in 1- or 2-ml fractions and analysed with ninhydrin. All the amino acids are determined separately by this technique.
H. F. W. KIRKPATRICK

4902. **Polychromatic technique for the identification of amino acids on paper chromatograms.** E. D. Moffat and R. I. Lytle (Div. of Biochem., Naval Medical Res. Unit. No. 4, U.S. Naval Training Center, Great Lakes, Ill.). *Anal. Chem.*, 1959, **31** (5), 926–928.—Apply the hydrochlorides of the amino acids to a strip of Whatman No. 1 filter-paper, develop with *n*-butanol - acetic acid - $H_2O$ (4:1:5) for 6 or 7 hr., and dry the strip at 105° for 5 min. Spray with a 50:3 mixture of a 0·2% soln. of ninhydrin in ethanol - acetic acid - 2:4:6-collidine (25:5:1) and a 1% soln. of $Cu(NO_3)_2.3H_2O$ in ethanol, dry the chromatogram at 105° for 1·5 or 2 min., and examine within 15 min. Twenty

common naturally occurring amino acids in quantities $> 1{\cdot}2$ $\mu$g are completely differentiated by their individual colours and $R_F$ values. A. R. ROGERS

4903. **Paper chromatography of amino acids and other organic compounds in selected solvents.** C. H. Edwards, E. L. Gadsden, L. P. Carter and G. A. Edwards (Dept. of Home Economics and Chem., Agric. and Tech. Coll. of N. Carolina, Greensboro, U.S.A.). *J. Chromatography*, 1959, **2** (2), 188–198.—$R_F$ values are given for 70 organic compounds in phenol - water (**I**) and butanol - propionic acid - water (**II**) systems and also for selected compounds in ethanol - acetic acid, butanol - ethanol - water, butanol - acetic acid - water, and ethanol. The influence of variations in temperature, the presence and absence of buffers and the presence of other compounds in the applied solution are reported. The oxidation of methionine to methionine S-oxide on the paper with **I** and **II** is discussed.
W. T. CARTER

4904. **Chromatography of neutral amino acids on columns of cellulose powder.** A. Iachan and J. C. Perrone (Nat. Technol. Inst., Rio de Janeiro, Brazil). *J. Chromatography*, 1959, **2** (2), 213–215.—The effect of the solvent composition on the separation of amino acids on columns of cellulose powder is demonstrated by using ethanol containing 5, 15 or 25% of water. It is concluded that the best separations are obtained by using gradient elution.
W. T. CARTER

4905. **Properties of ethyl esters of certain amino acids as related to artefacts in paper chromatography.** J. E. DeVay, A. R. Weinhold and G. Zweig (Univ. of California, Davis, U.S.A.). *Anal. Chem.*, 1959, **31** (5), 815–817.—L-Glutamic acid, L-aspartic acid, $\beta$-alanine, and $\gamma$-aminobutyric acid (but not other common amino acids), dissolved in 70% ethanol at pH $< 3$, form appreciable amounts of their (mono)ethyl esters within 36 hr., hence giving extra spots of higher $R_F$ value on chromatography with phenol - water ($R_F$ 0·88, 0·80, 0·83 and 0·80, respectively). Esterification did not occur in 70% ethanol at pH $> 3$, or in 10% *iso*propyl alcohol. The chromatography with phenol - water of unesterified glutamic or aspartic acid, at various pH values, gives double spots. Paper electrophoresis confirmed that these were due to dissociation into anions and cations. The changes are reduced to a minimum, or entirely prevented, by adjusting extracts of protein hydrolysates or plant materials to pH 5 after extraction.
D. G. MOSS

4906. **The compatibility of profile angles in the identification of substances. Application to the identification of asparagine.** A. C. Shead (Dept. of Chem., Univ. of Oklahoma, Norman, U.S.A.). *Mikrochim. Acta*, 1959, (3), 432–437 (in English).—A critical comparison of data on the angular profile values of asparagine which have been collected over half a century tends to confirm that these values are simply related geometrically and crystallographically. In the absence of distinctive chemical tests and the possibility of using the usual physical constants such as melting- and boiling-points, and the presence of water of crystallisation, one profile-angle measurement can serve for the calculation of all other compatible angles on related crystal forms. This gives promise for the solution of the problem of identification. D. F. PHILLIPS

4907. **Aldehyde oxidation. III. Succinaldehydic acid dehydrogenase. [Determination of $\gamma$-aminobutyrate and $\alpha$-oxoglutarate.]** W. B. Jakoby and E. M. Scott (Nat. Inst. of Arthritis and Metabol. Diseases, Bethesda, Md., U.S.A.). *J. Biol. Chem.*, 1959, **234** (4), 937–940.—Simple and specific assays are described for $1{\cdot}5 \times 10^{-5}$ to $1{\cdot}5 \times 10^{-4}$ *M* $\gamma$-aminobutyrate and $\alpha$-oxoglutarate. They depend on the use of $\gamma$-aminobutyric - glutamic transaminase coupled with succinaldehydic acid dehydrogenase and the amount of each substrate is determined from the increase in extinction at 340 m$\mu$ due to the formation of reduced triphosphopyridine nucleotide. The rate of reduction of the oxidised form is linear with respect to enzyme concn.
J. N. ASHLEY

4908. **$\gamma$-Amino-*n*-butyric, aspartic, glutamic and pyrrolidonecarboxylic acids: their determination and occurrence in grass during conservation.** H. T. Macpherson and J. S. Slater (Chem. Dept., King's Bldgs., Edinburgh Univ., Scotland). *Biochem. J.*, 1959, **71** (4), 654–660.—Glutamic and aspartic acids are determined in hot-water extracts of grass and silage by adsorption on a short column of De-Acidite FF in the acetate form, elution with dil. acetic acid, and assay in the eluate by ninhydrin colorimetry according to the method of Hirs *et al.* (*J. Amer. Chem. Soc.*, 1954, **76**, 6063). Pyrrolidonecarboxylic acid is determined after hydrolysis to glutamic acid. It is eluted from the column with 5% (v/v) formic acid soln. and after evaporation of the eluate the residue is heated with 6 *N* HCl to convert the cyclic acid into glutamic acid. For the determination of $\gamma$-aminobutyric acid the sample is applied to a column of Zeo-Karb 225 in the pyridine form. The acid is eluted with 0·2% (v/v) pyridine soln. and determined by the ninhydrin colorimetric method.
J. N. ASHLEY

4909. **Colorimetric determination of urea with special reference to the arginine determination.** Yukiaki Nadai (Dept. of Med. Chem., Fac. of Med., Kyoto Univ.). *Acta Med. Univ. Kioto*, 1959, **36** (1), 1–5 (in English).—To determine the arginase activity of mouse liver and kidney homogenate, mix the enzyme soln. (1 ml) with 0·05 *M* arginine of pH 6 (1 ml), *M* barbitone buffer of pH 9·2 (1 ml) and 0·01 *M* $MnSO_4$ (1 ml) and incubate under toluene at 37°. Add 10% trichloroacetic acid soln. (6 ml), set aside for 10 min. and filter. To 5 ml of filtrate, containing 0·15 to 1·6 mg of urea, add a mixture of 2% *p*-dimethylaminobenzaldehyde in 95% ethanol - conc. HCl (20:3) (2 ml), set aside at room temp. for 15 min. and measure the extinction at 450 m$\mu$ in a 3-cm cell.
A. R. ROGERS

4910. **Identification and determination of 5-hydroxyindol-3-ylacetic acid.** H. Wachsmuth and L. van Koeckhoven (Hôp. Stuivenberg, Anvers, Belgium). *Clin. Chim. Acta*, 1959, **4** (3), 438–443.—Extraction and chromatography are carried out by the method of Udenfriend *et al.* (*J. Biol. Chem.*, 1955, **216**, 499). Reactions with $FeCl_3$ - $K_3Fe(CN)_6$, vanillin, 1:4-naphthaquinone and xanthhydrol are described.
H. F. W. KIRKPATRICK

4911. **Quantitative spectrophotometric determination of 5-hydroxytryptamine and 5-hydroxyindol-3-ylacetic acid.** A. Carcasona, J. Cervós-Navarro and F. Unterharnscheidt (Inst. f. Neuropath. der Univ., Bonn, Germany). *Klin. Wochschr.*, 1959, **37** (5), 253–254.—A modification of the method of

Udenfriend *et al.* (*cf. Anal. Abstr.*, 1956, **2**, 1449) is proposed. To the acid soln. (1 ml) freed from interfering substances add 0·1% ethanolic 1-nitroso-2-naphthol soln. (0·5 ml) and 0·0139 *M* $HNO_2$ (0·5 ml), warm to 50° to 60° to speed the reaction, and extract the excess of reagent with 1:2-dichloroethane. Measure the violet colour at 540 mμ against a blank taken through the same process. Prepare a standard curve with 5-hydroxytryptamine soln. containing 5 to 80 μg per ml; 5-hydroxyindol-3-ylacetic acid is determined similarly, the excess of reagent being extracted with ethyl acetate (2 × 5 ml). H. F. W. KIRKPATRICK

4912. **Determination in urine of some metabolites of tryptophan—kynurenine, anthranilic acid and 3-hydroxyanthranilic acid—and reference to the presence of o-aminophenol in urine.** S. L. Tompsett (Dept. of Clin. Chem., Univ. of Edinburgh, Scotland). *Clin. Chim. Acta*, 1959, **4** (3), 411–419.—Kynurenine is separated by distillation and determined by the diazotisation and coupling procedure of Bratton and Marshall. *o*-Hydroxyamines are separated by extraction with diethyl ether and determined with 2:6-dichloro-*p*-benzoquinone-4-chlorimine.
H. F. W. KIRKPATRICK

4913. **Protein determination for large numbers of samples.** G. L. Miller (Pioneering Res. Div., Quartermaster Res. and Engng Center, Natick, Mass., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 964.—The procedure of Lowry *et al.* (*J. Biol. Chem.*, 1951, **193**, 265) has been modified. The reproducibility of the results is about the same as in the original test, but the time taken per analysis is substantially reduced. *Procedure*—Add 1 ml of a mixture (10:1) of a 10% soln. of $Na_2CO_3$ in 0·5 *N* NaOH with a 0·5% soln. of $CuSO_4$ in 1% K tartrate soln. to the sample of protein soln. (1 ml), and after 10 min. add diluted Folin phenol reagent (1:11) (3 ml) with sufficient force to ensure mixing. Heat the soln. at 50° for 10 min., then cool, and measure the colour. A. R. ROGERS

4914. **Stoicheiometry in the estimation of disulphide in intact proteins using mercuric chloride.** S. J. Leach (C.S.I.R.O., Parkville, Melbourne, Victoria, Australia). *Biochim. Biophys. Acta*, 1959, **33** (1), 264–266.—The method is based on the titration of soluble proteins with $HgCl_2$ soln. at pH 9 in the presence of excess of sulphite and of urea (8 *M*). The end-point is detected amperometrically with a dropping mercury electrode. Both disulphide and mercapto groups react, and the result requires correction for thiols, which are determined separately by a polarographic method. For insoluble proteins (*e.g.*, wool), excess of $HgCl_2$ is added and complete reaction is obtained in the presence of 8 *M* urea in 18 hr. The thiol content is then calculated by the described method from the observed initial, final and blank diffusion currents at −1·0 V *vs.* the S.C.E. W. H. C. SHAW

4915. **Rapid method for the determination of total protein in serum and plasma with Amido black 10B.** A. Basso and G. Batacchi (Ist. di Clin. Chirurg. Gen., Florence Univ.). *Biochim. Appl.*, 1959, **6** (2), 65–73.—The staining - elution technique with Amido black 10B (C.I. Acid Black 1) used for the quant. determination of protein fractions in paper electrophoresis is modified for the rapid determination of total protein by applying it to a single spot of serum or plasma on paper. The extinction of the eluate at 620 mμ is converted to protein content by means of a standard graph similarly prepared from human serum which has been analysed by Kjeldahl's method.
E. C. APLING

4916. **Interaction between dyes and serum proteins in paper electrophoresis. Some quantitative problems.** V. Scardi and V. Bonavita (Inst. of Human Physiol., Univ. of Naples, Italy). *Clin. Chim. Acta*, 1959, **4** (3), 322–328.—The different dye-binding capacities of the albumin and globulins of serum is confirmed in experiments with dyes commonly used in paper electrophoresis. Quant. evaluation is better carried out by determining the albumin and total globulins by chemical means (*e.g.*, with biuret), and limiting the calculation of the pattern to the value of the globulin fractions expressed as percentages of the total globulin content. H. F. W. KIRKPATRICK

4917. **Investigation of the correlation between the results of electrophoresis of serum proteins on paper, on starch gel and by immuno-electrophoresis.** J. Moretti, G. Boussier, M.-P. Hugou and L. Hartmann (Lab. de Biochim., Fac. de Méd., Paris). *Bull. Soc. Chim. Biol.*, 1959, **41** (1), 79–87.—Several pathological sera have been examined by each of the three techniques. Immuno-electrophoresis gives 19 lines of precipitation, 11 of which have been identified; 18 bands are detected by starch-gel electrophoresis. The correlation of these with the 5 zones seen on paper electropherograms has been established. With immuno-electrophoresis the resolution is rather better than on starch gel. Lipoproteins are not shown up by Amido black 10B (C.I. Acid Black 1) in the latter technique, and only poorly by Sudan black B (C.I. Solvent Black 3), while more components of the α- and β-globulins can be demonstrated by immuno-electrophoresis. In clinical work the choice of technique will possibly be governed by the type of abnormality to be assessed. D. W. MOSS

4918. **Rapid methods for estimating some serum proteins and the significance of abnormal results.** G. Discombe (Central Middlesex Hospital, London). *Lancet*, 1959, **i**, 619–621.—Total serum protein is determined by the method of Phillips *et al.* (1945), in which a graded series of $CuSO_4$ soln. of known sp. gr. is used to determine the serum sp. gr. This method is rapid, and accurate to ± 0·18 g per 100 ml. Serum albumin is measured by the method of Bracken and Klotz (*Amer. J. Clin. Path.*, 1953, **23**, 1055), which is based on the protein error of indicators, as determined by the change in extinction at 550 mμ of a soln. of methyl orange in the presence of serum. A standard curve is prepared from human or bovine albumin, and covers a range of 1% to 6%; α-, β- and γ-globulins do not interfere, but haemolysis, turbidity and sera from cases of severe jaundice give erroneously low results. Serum γ-globulin is determined by a modification of the $ZnSO_4$ - turbidity method of Kunkel (*Proc. Soc. Exp. Biol. Med.*, 1947, **66**, 217), the $ZnSO_4$ reagent being stored out of contact with $CO_2$, and the serum sample being added to the reagent with a teat-pipette. The results are expressed in terms of Kunkel's $BaSO_4$ units. Fibrinogen is determined by the method of Stirland (*Lancet*, 1956, **i**, 672). A mixture of plasma and 1% NaCl soln. is heated for 15 min. at 56°, then cooled, and the extinction measured at 660 mμ. Results are expressed as Kunkel units (1 Kunkel unit ≡ 42·8 mg of fibrinogen per 100 ml). For values of >20 units, less plasma must be used.

Each of these methods can be applied to 20 to 30 sera by one technician in a normal working afternoon. The variations in individual serum-protein values and also abnormal distribution patterns in various diseases are discussed. D. B. PALMER

4919. **Borate buffer in zone electrophoresis.** R. Havez and G. Biserte (Lab. de Chim. Biol., Fac. Mixte de Méd. et de Pharm., Lille, France). *Clin. Chim. Acta*, 1959, **4** (3), 334–339.—The influence of the borate buffer in the method of Smithies (*Biochem. J.*, 1955, **61**, 629) in changing the speed of migration of the serum proteins is attributed to interaction of protein and borate ions. The pre-albumin fractions are identified by immunological techniques. H. F. W. KIRKPATRICK

4920. **Ethanediol and propane-1:2-diol in the pre-staining of lipoproteins for electrophoresis.** H. J. McDonald and L. P. Ribeiro (Grad. Sch. and Stritch Sch. of Med., Loyola Univ., Chicago, Ill., U.S.A.). *Clin. Chim. Acta*, 1959, **4** (3), 458–459.—Prepare a soln. of Sudan black B (C.I. Solvent Black 3) by heating ethanediol or propane-1:2-diol to 100° to 110°, adding 1% of dye, stirring for 5 min. and filtering hot through Whatman No. 2 filter-paper. After cooling to room temp., filter the soln. again. To 0·5 ml of serum add slowly with constant gentle mixing 0·1 ml of dye soln. Set aside at room temp. for 45 min., then centrifuge to remove the excess of dye. Use $\simeq 10$ µl of the treated serum per cm width of Whatman 3MM paper for the electrophoresis. These conditions give quant. results in accordance with the Beer - Lambert law. H. F. W. KIRKPATRICK

4921. **Demonstration of plasma fibrinogen by paper electrophoresis.** G. A. Cheyne [Obstet. Med. Res. Unit (M.R.C.), Univ. of Aberdeen, Scotland]. *Lancet*, 1959, **i**, 763.—Electrophoresis of heparinised plasma is carried out by the usual procedure at 8 mA for 24 hr. The polarity is then reversed and the current increased to 12 mA for 1·5 hr. This method yields good separation of the fibrinogen band from other globulins.
H. F. W. KIRKPATRICK

4922. **Determination of fibrin by the heating method of Schulz.** H. Dittrich, E. Puffer and E. Seifert (I Med. Abt. d. Hanusch-Krankenhauses, Vienna, Austria). *Klin. Wochschr.*, 1959, **37** (8), 465–469.—A critical study is made of the method, and the factors influencing the results are investigated. Experiments with pure fibrinogen soln. show variations in the results with different solvents and different quantities of reagents. Under suitable conditions the method has useful clinical application.
H. F. W. KIRKPATRICK

4923. **Isolation and estimation of the sugar of pyrimidine nucleosides and nucleotides after reduction.** L. Haavaldsen, S. Laland, J. M. McKee and E. Roth (The Univ., Blindern, Oslo, Norway). *Biochim. Biophys. Acta*, 1959, **33** (1), 201–206.—The preliminary reduction of pyrimidine nucleotides and nucleosides with sodium amalgam and water permits the subsequent hydrolysis with 0·1 *N* HCl at 100° for 15 min. to be carried out almost quantitatively with respect to sugar. The orcinol or diphenylamine colorimetric methods may then be applied to the determination of the sugar, which may also be characterised by paper chromatography or electrophoresis. The application of the method to thymidine, deoxycytidine and deoxycytidylic and thymidylic acids is described. W. H. C. SHAW

4924. **Interference of phenols in the fluorimetric determination of nucleotides.** A. M. Mayer (Low Temp. Res. Sta., Cambridge, England). *Experientia*, 1959, **15** (4), 158 (in English).—Phenolic substances present in plant tissues cause an apparent loss of phosphopyridine nucleotides when they are determined by the fluorimetric procedure of Lowry *et al.* (*J. Biol. Chem.*, 1957, **224**, 1047). Substances such as catechol, phloroglucinol and quinol have a quenching effect on the fluorescence, while compounds which fluoresce themselves, such as caffeic acid, can cause an apparent reduction in the fluorescence of diphosphopyridine nucleotide in strong alkali. It is concluded that this method cannot be applied to any tissue in which such phenolic compounds are likely to occur, especially since the amounts of, and ratios between, various phenols in plant tissues are liable to change markedly during the development of the plant.
P. NICHOLLS

4925. **Rapid paper-chromatographic micro-assay of free and ester cholesterol of blood.** M. L. Quaife, R. P. Geyer and H. R. Bolliger (Dept. of Nutrition, Harvard Sch. of Public Health, Boston, Mass., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 950–955.—After the extraction of serum by acetone - ethanol (1:1), an aliquot of the filtrate is evaporated to dryness, and dissolved in $CHCl_3$. An aliquot (10 to 20 µl, containing 15 to 75 µg each of free and esterified cholesterol) is spotted on strips of Whatman No. 1 paper impregnated with $ZnCO_3$, and chromatographed by the ascending technique, with 1·5% diethyl ether in *cyclo*hexane as the mobile phase. Standards of cholesterol and cholesteryl oleate are run simultaneously. The solvent front is allowed to ascend about 12 cm (20 to 30 min.). After location on a guide strip with molybdophosphoric acid, the segments containing the free and esterified cholesterol are cut out, and eluted with $CHCl_3$. Cholesterol is determined by a modification of the method of Zlatkis *et al.* (*J. Lab. Clin. Med.*, 1953, **41**, 486). The results for total cholesterol agreed within 2% with those by two other methods. D. G. MOSS

4926. **Spectrophotometric determination of residual $\Delta^4$-3-oxosteroids in bulk $\Delta^{1:4}$-3-oxosteroids. Differential rates of thiosemicarbazone formation.** A. A. Forist (Dept. of Phys. and Anal. Chem., The Upjohn Co., Kalamazoo, Mich., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 913–915.—The method is based on the difference in the rates of thiosemicarbazone formation, $\Delta^{1:4}$-3-oxosteroids reacting only slowly under the conditions given. Results for 12 mixtures containing $< 6\%$ of $\Delta^4$-3-oxosteroid showed a mean deviation of $\pm$ 0·04% absolute. *Procedure*—Mix a soln. of the sample (0·5 mg) in 95% ethanol (5 ml), previously brought to 25°, with 0·1 *M* thiosemicarbazide hydrochloride (1 ml), also at 25°; set aside at 25° for 120 $\pm$ 2 min., then measure the extinction at 302 mµ against a reagent blank. The extinction is a linear function of the percentage of $\Delta^4$-3-oxosteroid, but for maximum accuracy the calibration curve should be checked at the same time as the analysis.
A. R. ROGERS

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*See also Abstracts*—**4758**, Determination of F in biological media. **4934**, Lipids in tobacco. **4935**, Determination of adrenaline. **4956**, Determination of cystine. **4968**, HCN in blood and urine. **5028**, Artefacts in paper chromatography of amino acids. **5030**, Chromatography of amino acids. **5053**, Determination of enzyme activity.

## Pharmaceutical analysis

4927. **Application of paper chromatography to the detection of alkaloids in toxicological food analysis.** J. Kolankiewicz and M. Nikonorow (Dept. of Food Res., Inst. of Hygiene, Warsaw). *Acta Polon. Pharm.*, 1959, **16** (2), 115–122.—The paper-chromatographic method for the detection of alkaloids, *e.g.*, codeine, veratrine, quinine and narcotine, in several foods (a 100-g sample) is described. For the preliminary extraction of the alkaloids add to the sample 300 ml of ethanol acidified to litmus paper with HCl. Digest on a water bath at 40° for 24 hr., filter and retain the filtrate. Add 100 ml of acidified ethanol to the residue, digest for another 12 hr. and filter again. Combine the filtrates and remove the alcohol by evaporating on a water bath at 40°. Add 30 ml of water and extract with diethyl ether (5 × 50 ml). Add NaOH soln. to the aq. layer till it is alkaline to litmus and extract with diethyl ether (5 × 50 ml). Evaporate the ether extract to 50 ml, transfer it to a separating-funnel and wash with 2 *N* HCl (3 × 20 ml). To the combined acid washings add NaOH till they are alkaline to litmus and extract with diethyl ether (3 × 50 ml). Evaporate the ether completely and dissolve the extract in 5 ml of ethanol. Retain this alcoholic soln. for chromatography by the descending technique on Whatman No. 1 paper. Apply drops of the test and standard soln. to the paper and impregnate its whole area above the starting line with a freshly prepared ethanolic soln. of formamide (1:1). Dry the paper between two filter-papers, then at 40° for 30 min. Spray the starting points with the ethanolic soln. of formamide (1:1) and after 10 min. transfer the paper to a glass container containing $CHCl_3$ at 25°. The development is complete in 2·5 hr. Dry the chromatogram at 105° and spray with a soln. of potassium iodoplatinate, washing off the excess with water in order to observe the spots on the white background. The following amounts of alkaloids can be detected—codeine 0·01 to 0·3 mg, quinine 0·005 to 0·015 mg, veratrine 0·1 to 0·15 mg and narcotine 0·05 to 0·075 mg. W. Roubo

4928. **Determination of the origin of opium. II. Simultaneous assay of narcotine, thebaine and papaverine in opium by infra-red spectroscopy.** V. J. Bakre, Z. Karaata, J. C. Bartlet and C. G. Farmilo (Food and Drug Directorate, Dept. of Nat. Health and Welfare, Ottawa, Ontario, Canada). *J. Pharm. Pharmacol.*, 1959, **11** (4), 234–243.—Triturate the sample (4·5 g as 20 to 40-mesh powder) for 10 to 20 min. with glacial acetic acid (20 ml), slowly add $H_2O$ (25 ml) with continuous stirring and filter through paper. Extract a 10-ml aliquot of the filtrate with $CHCl_3$ (4 × 10 ml). Wash each extract successively with $H_2O$ (10 ml), 0·2% sodium bisulphite in 30% aq. NaOH soln. (25 ml), $H_2O$ (10 ml) and $H_2O$ (10 ml). Filter the combined $CHCl_3$ soln. through cotton wool and evaporate. Dry the residue in a desiccator, mix it with anhydrous $CCl_4$, filter through sintered glass and dilute the filtrate to 25 ml. Examine the i.r. spectrum from 1100 $cm^{-1}$ to 1900 $cm^{-1}$ in a 1-mm sodium chloride cell. Calculate the percentages of narcotine, thebaine and papaverine from the extinctions at 1767, 1602 and 1160 $cm^{-1}$. The results for 7 samples of opium were compared with those obtained by the United Nations K/34 method and a modified method (*cf.* Lee and Farmilo, *Anal. Abstr.*, 1959, **6**, 1888). The proposed i.r. method needs only half a day per sample, and the reproducibility is two or three times as good as that of the chemical methods. A. R. Rogers

4929. **Determination of small amounts of hyoscyamine and hyoscine in crude drugs.** J. W. de Bruyn and J. G. van Hall (Inst. v. Vered. van Tuinbouw., Wageningen). *Pharm. Weekbl.*, 1959, **94** (8), 262–269.—The alkaloids are separated by paper chromatography with the solvent *n*-butanol - glacial acetic acid (10:1) saturated with water. The spots are eluted and the alkaloids are determined by the method of Häussler (*Anal. Abstr.*, 1958, **5**, 1662) by measurement of the coloured complex with Tropaeolin OO (C.I. Acid Orange 5). Quantities of 10 to 150 μg can be determined. Hyoscyamine can be determined with methyl orange at pH 8; hyoscine does not react. N. E.

4930. **Assay of strychnine in pharmaceutical preparations of nux vomica.** I. S. Taylor and A. Ifrim (Commonwealth Lab., Melbourne, C.I.). *J. Pharm. Pharmacol.*, 1959, **11** (3), 191.—Render alkaline an aliquot of the sample (containing ≃ 0·5 mg of strychnine) and evaporate to a vol. of ≃ 2 ml. Mix the residue with active alumina (heat alumina at 800° for 6 hr.) (1 g) and transfer to a chromatographic column of active alumina (10 g) packed "wet" with ethanol. Elute with ethanol (50 ml) at a rate of 5 to 10 drops per min. and allow the column to drain. Evaporate the eluate to dryness, dissolve the residue in *N* $H_2SO_4$ (100 ml) and measure the extinction at 262 mμ (*A*) and 300 mμ (*B*) against *N* $H_2SO_4$ in 1-cm quartz cells. Then strychnine (%) = (0·318 *A* − 0·460 *B*)/100. A. R. Rogers

4931. **Determination of ephedrine in ephedra by non-aqueous titration.** Yun-Han Ho and Teng-Han Tang. *Acta Pharm. Sinica*, 1959, **7** (3), 119–121.—The simplified titrimetric method in non-aqueous soln. (*cf.* Chatten and Pernarowski, *Anal. Abstr.*, 1954, **1**, 1626) is suitable for the determination of ephedrine in ephedra and is applicable to ephedrine tablets and ampoules. *Procedure*—Weigh out finely powdered ephedra (10 g) into a 500-ml stoppered flask, add 1 *N* HCl (40 ml) and heat on a water bath for 1 hr. After cooling, neutralise with 6 *N* NaOH and add $CHCl_3$ (100 ml). Stopper the flask and shake vigorously for 15 min. Add powdered tragacanth (6 g) and shake for a further 5 min. Filter and transfer the $CHCl_3$ filtrate (50 ml ≡ 5 g of sample) to a clean flask. Add 6% mercuric acetate soln. (5 ml) and 0·5% crystal violet indicator (1 drop) and titrate with 0·1 *N* $HClO_4$ in glacial acetic acid until the colour changes to green. The results for 3 samples by the method described are in agreement with those obtained by the method of the Chinese Pharmacopoeia, 1953. S. H. Yuen

4932. **Stability of rescinnamine in solution.** The Pharmaceutical Society of Great Britain and The Society for Analytical Chemistry (Anal. Methods Committee, 14 Belgrave Sq., London). *J. Pharm. Pharmacol.*, 1959, **11** (4), 211–215.—Results of an investigation by a Joint Committee on Methods of Assay of Crude Drugs are presented. The u.v. absorption characteristics of rescinnamine change when soln. in various solvents are exposed to daylight, but there is no detectable alteration in the pharmacological properties. Soln. of trimethoxycinnamic acid, but not of trimethoxybenzoic acid, show similar changes. It appears that the method of assay of rauwolfia proposed by Carol *et al.* (*cf. Anal. Abstr.*, 1956, **3**, 2847) cannot be regarded as trustworthy. A. R. Rogers

4933. **Photometric micro-determination of lupin alkaloids.** M. Wiewiórowski and J. Skolik (Inst. f. allg. Chem., Ökonom. Hochsch., Poznań). *Roczn. Chem.*, 1959, **33** (2), 461–469 (in German).—The method permits the separation and determination of $\simeq$ 20-$\mu$g quantities of lupinine, lupanine, hydroxylupanine, angustifoline and sparteine with an error $< \pm 3\%$. *Procedure*—Moisten the crushed seeds (300 to 400 mg) with 2 *N* KOH (6 drops), mix with kieselguhr (600 mg) and pack into a column for chromatography. Elute with $CHCl_3$ (9 ml) so that the eluate drips on to filter-paper. Allow the $CHCl_3$ to evaporate, acidify the extracted spot with acetone - acetic acid - $H_2O$ (10:1:6) and dry the paper over KOH and $P_2O_5$ *in vacuo*. Wash the alkaloids on to a paper chromatogram with methanol and develop with $H_2O$-satd. *n*-butanol. Dry the paper and expose it to iodine vapour to reveal the positions of the separated alkaloids. Cut out the zones and extract each separately with $H_2O$ (3 ml). Add a 0·0002 *M* soln. of bromothymol blue in borate buffer (pH 8·0) (5 ml) to the aq. extract and shake for 5 min. with $CHCl_3$ (10 ml). Mix 5 ml of the $CHCl_3$ layer with 0·002 *N* methanolic KOH (5 ml) and measure the extinction in a Lange colorimeter with an orange filter OG2.

A. R. ROGERS

4934. **Estimation of the lipid fractions of tobacco.** D. N. Hellier (Res. Dept., Carreras Ltd., 221 Stanhope St., London). *Chem. & Ind.*, 1959, (8), 260–261.—Absolute ethanol is found to be more effective than light petroleum for the extraction of tobacco when determining tobacco resins. *Procedure*—Dry ground tobacco (30 g) is extracted in a Soxhlet apparatus for 10 hr. with 150 ml of ethanol. The extract is concentrated to 100 ml and 5 ml is streaked on to Whatman No. 3 paper. Water-soluble compounds are removed by descending chromatography with 2% aq. acetic acid. After air-drying, the base-line strip is eluted successively with light petroleum, diethyl ether and ethanol to give "soft resin", "hard resin A" and "hard resin B" fractions, respectively. Analyses for various growing areas are given, and the contents of the various fractions are discussed. E. J. H. BIRCH

4935. **Micro-determination of adrenaline by titration of the ferrocyanide formed from ferricyanide.** J. A. C. van Pinxteren and M. E. Verloop (Farm. Lab., Rijksuniv., Utrecht, Holland). *Pharm. Weekbl.*, 1959, **94** (6), 169–178.—Adrenaline is quant. oxidised with $K_3Fe(CN)_6$ to adrenochrome, and the resulting ferrocyanide is determined by a dead-stop end-point titration with 0·015 *M* $ZnSO_4$. The results are vitiated by the presence in pharmaceutical preparations of sodium metabisulphite and phenol; these substances are eliminated by passing a current of N through the test sample (2 ml), slightly acidified with dil. $H_2SO_4$, for 10 min. at 100°. The cooled sample is then neutralised and mixed with aq. 2% $Na_2B_4O_7$ soln. (2 ml); at the resulting pH (7·6 to 9·3), the time for oxidation with $K_3Fe(CN)_6$ (5 ml of 0·05 *M* soln.) is reduced to 5 min. The soln. is slightly acidified before titration. The results show good reproducibility and are $\gtrsim$2% high. P. S. ARUP

4936. **Quantitative analysis of senna leaf by chemical methods.** M. Henneberg (Zaklad Anal. i Technol. Leku Roslinnego). *Biul. Inst. Roślin Leczniczych*, 1959, **5** (1), 1–10.—To establish the most suitable method for the quant. determination of the active principle of senna leaf two chemical methods were compared, and after modification, in particular to the method of extraction, Auterhoff's method (*Arzneimittel-Forsch.*, 1951, **1**, 412) was considered to have some advantages over Kussmaul and Becker's method (*Helv. Chim. Acta*, 1947, **30**, 59), especially for a series of determinations, as it is much shorter, simpler and sufficiently accurate in comparison with pharmacological estimations. On the basis of results obtained by chemical and pharmacological methods, it is proposed that the minimum content of sennosides in senna leaf should be 2·2%. W. B. MIASKOWSKI

4937. **Determination of anthraquinone derivatives in proprietary medicines. I. Photometric determination of frangula emodin in Cholagol.** L. Kraus (State Inst. for Control of Drugs, Prague). *Českosl. Farm.*, 1959, **8** (2), 83–84.—The method is based on the classical Bornträger reaction with KOH and was applied to Cholagol (a mixture of frangula emodin, curcumin, volatile oils, ethanol and olive oil). *Procedure*—Boil the sample (approx. 1 g $\equiv$ 0·15 mg of emodin) for 20 min. under reflux with NaOH soln. (20%) (20 ml), then heat slightly for 5 to 8 min. and filter the pink soln. into a 100-ml flask. Wash the filter with NaOH soln. (20%) (20 ml) into a beaker and warm the filtrate. Repeat this procedure three times. Cool the combined filtrates, dilute to vol. with NaOH soln. (20%), mix, and measure the extinction in a 5-cm cell with the use of filter S53. Compare with a calibration curve. J. ZÝKA

4938. **Polarography of santonin.** Shu-Hao Tian and Tong-Hui Chow. *Acta Pharm. Sinica*, 1959, **7** (1), 17–24.—Pure santonin is studied in different buffers. It is found that, below pH 3·5, only one wave is obtained, corresponding to a one-electron reversible reduction; the $E_{\frac{1}{2}}$ shifts more and more towards the negative with increasing pH. In the range pH 3·5 to 9, two waves are observed, the first being the same as that found below pH 3·5 and the second is a one-electron irreversible reduction. At pH values $> 9$, the first wave merges into the second one, resulting in a single wave corresponding to a two-electron reduction. The effects of the mercury height and temp. on the limiting current show that the latter is diffusion-controlled. For the analysis, a medium containing ethanol (25% v/v) and a buffer (boric acid - KCl - NaOH) (pH 10) are recommended. The wave height is measured at $-1{\cdot}7$ V *vs.* the S.C.E. Santoninic acid behaves similarly to santonin with slightly higher negative $E_{\frac{1}{2}}$, but santonic acid formed by the vigorous treatment of santonin with alkali is polarographically inactive. From the results given by pure santonin and from a study of the extraction of santonin from artemisia, a procedure for the rapid analysis of artemisia is proposed. The sample may be analysed in about 90 min. and the results agree with those obtained by the gravimetric method. SCI. ABSTR. CHINA

4939. **Methods for the determination of tannins.** K. Herrmann and W. Enge (Inst. f. Landwirts. Technol. u. Vorratspflege, Martin Luther Univ., Halle-Wittenberg, Germany). *Dtsch. ApothZtg.*, 1959, **99** (14), 325–328.—Results for tannins in vegetable drugs obtained by the routine iodimetric method (in which the oxidative value of the extract is determined before and after the removal of the tannins) and by the colorimetric tungstophosphate method are generally in good agreement with those obtained by the standard gravimetric method;

results obtained by the Cu acetate gravimetric method are from 7 to 19% low. All the available methods are subject to possible errors due to the inclusion of certain non-tannins (chiefly polyhydric phenols) in the determinations. Specific methods should be developed for the separate determination of such substances. (35 references.) P. S. ARUP

4940. **Titration of alkali salts of organic acids with perchloric acid in non-aqueous medium.** M. Rink, R. Lux and E. Franken (Pharmaceut. Inst., Bonn Univ., Germany). *Dtsch. ApothZtg*, 1959, **99** (7), 157–158.—Several alkali and alkaline-earth salts of organic acids, contained in D.A.B. VI, were determined by titration with 0·1 *N* $HClO_4$ in glacial acetic acid, with Oracet blue B (C.I. Solvent Blue 19) as indicator. The method is similar to that for the determination of organic bases (*cf.* Rink *et al.*, *Anal. Abstr.*, 1959, **6**, 1885).
M. H. SAWISTOWSKA

4941. **Determination of barbiturates in tablets.** M. Béguin (Lab. de Pharm. Galénique, Univ., Genève). *Pharm. Acta Helv.*, 1959, **34** (3), 146–161 (in French).—Grind and extract the powdered sample (containing 0·6 to 0·9 g of barbiturate) with 2 *N* aq. $NH_3$ (4 × 9 ml). For a sodium barbiturate, use 0·5 *N* aq. $NH_3$; for calcium cyclobarbitone, use six 8-ml portions of 2 *N* aq. $NH_3$. Centrifuge each extract and dilute the combined soln. to 50 ml. Acidify a 25-ml aliquot of the soln. with 5 *N* HCl and extract with $CHCl_3$ (3 × 25 ml). For phenobarbitone, use $CHCl_3$ - diethyl ether (4:1) (3 × 25 ml); for calcium cyclobarbitone, $CHCl_3$ (4 × 25 ml). Evaporate the combined extracts, dry the residue at 103° to 105° and weigh. If the excipient contains sodium carboxymethylcellulose, extract the powdered sample with 95% ethanol, evaporate the extract and assay the residue. Remove Carbowax 6000 by shaking the ammoniacal soln. with $CHCl_3$ - diethyl ether (4:1) before the addition of HCl. Benzoic acid and its salts interfere, but cannot be removed. The precision of the method is ±0·5 to 1·5%. A. R. ROGERS

4942. **X-ray diffraction patterns of *p*-nitrobenzyl derivatives of barbituric acids.** J. A. R. Cloutier and J. M. Manson (Dept. of National Health and Welfare, Ottawa, Ontario, Canada). *Appl. Spectroscopy*, 1959, **13** (2), 34–38.—Diffraction data for the *p*-nitrobenzyl derivatives of 20 clinically important barbituric acids are presented.
K. A. PROCTOR

4943. **Coulometric micro-titration of thiopentone sodium and of rivanol [ethacridine lactate].** K. Kalinowski and A. Piotrowska (Dept. of Pharm. Chem., Med. Acad., Lódź). *Acta Polon. Pharm.*, 1959, **16** (2), 107–109.—The determination of thiopentone sodium (**I**) and ethacridine lactate (**II**) with the help of electrically generated Br is described. The dead-stop method was used with two platinum electrodes in a specially constructed cell. *Determination of* **I**—Add to the anode compartment 3 ml of 30% KBr soln., 3 ml of 10% HCl soln. and 2 ml of the test soln. and make up to 30 ml with water. To the cathode compartment add several ml of 10% HCl soln. so that its level is higher than that in the anode compartment. Switch on the mixing device in the anode compartment, then the indicating circuit and finally the generating system and measure the time from this point every 0·2 sec. Continue the electrolysis till the presence of free Br is indicated. Carry out a blank determination with water instead of the test soln. A current of 8 mA is used. *Determination of* **II**—Add to the anode compartment 5 ml of 20% KBr soln., 5 ml of 15% $H_2SO_4$ soln. and 2 ml of the test soln. and make up to 25 ml with water. To the cathode compartment add 15% $H_2SO_4$ soln. till its level is higher than that in the anode compartment and then proceed as for **I**. The amount of each substance is calculated from the equation given. The method permits the determination of from 0·3 to 1·5 mg of **I** with ± 0·7% accuracy, and of 1 to 3 mg of **II** with ± 1% accuracy. It takes only a few minutes, is simple and needs only a small amount of sample.
W. ROUBO

4944. **Spectrophotometric determination of methadone.** M. J. Pro (Alcohol and Tobacco Tax Div. Lab., Int. Rev. Service, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1959, **42** (1), 117–180.—Methadone is extracted from tablets with water and the extinction of the soln. at 292·5 mμ is read. Alternatively, the sample may be extracted with $CHCl_3$ and the extinction read at 5·86 μ. The procedure for the separation of methadone from interfering substances is described.
A. A. ELDRIDGE

4945. **Micro-method for the estimation of anaesthetics derived from aminobenzoic acid. Procaine hydrochloride and tetracaine [amethocaine] hydrochloride combined in cartridges for dental anaesthesia.** M. E. Auerbach and M. M. Tuckerman (Sterling-Winthrop Res. Inst., Rensselaer, N.Y., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1959, **48** (3), 194–196.—Mix the sample [1 ml containing 20 mg of procaine hydrochloride (**I**) and 1·5 mg of amethocaine hydrochloride (**II**)] with $H_2O$ (20 ml) and 10% $Na_2CO_3$ soln. (2 ml) and extract with $CHCl_3$ (3 × 25 ml). Wash the combined extracts with $H_2O$ (15 ml), filter through paper, add 7 *N* ethanolic HCl (0·2 ml), evaporate to dryness and dissolve the residue in $H_2O$ (100 ml). Determine the total anaesthetic in a 25-ml aliquot by dilution with 7 *N* $H_2SO_4$ to 50 ml and measurement of the extinction at 272 mμ. To determine **II** alone, mix a 50-ml aliquot with 7% $NaNO_2$ soln. (1 ml) and add *N* HCl (1 ml). After 5 min., add 10% $Na_2CO_3$ soln. (2 ml) and 1% Na 8-amino-1-naphthol-2:4-disulphonate soln. (2 ml), set aside for 1 min. and extract with $CHCl_3$ (3 × 25 ml). Wash the combined extracts with $H_2O$ (15 ml), filter through paper, dilute with $CHCl_3$ to 100 ml and measure the extinction at 290 mμ against a blank prepared by similar treatment of a 0·02% soln. of **I** (50 ml).
A. R. ROGERS

4946. **New method for the colorimetric determination of sodium 4-aminosalicylate.** G. Baiulescu (Chem. Res. Centre, Bucharest). *Acad. R.P.R., Stud. Cercet. Chim.*, 1959, **6** (3), 433–438.—The method is based on the formation of an orange-coloured complex with uranyl ions which obeys the Beer - Lambert law. A soln. of uranyl nitrate (2·5% in methanol) is used as reagent, and a 0·3% soln. of Na 4-aminosalicylate (**I**) for preparing the standard curve. The maximum absorption is at 420 mμ. A Pulfrich photometer with S42, S43 and S47 filters is used. Under the conditions given, the determination of 0·75 to 6 mg of **I** is not affected by the presence of 1 mg of isoniazid nor by *m*-aminophenol.
H. SHER

4947. **Photometric determination of some derivatives of salicylic acid.** O. Hrdý and J. Černý (State Inst. for Control of Drugs, Prague), *Ceskosl. Farm.*, 1959, **8** (2), 73–77.—The method is based on the

condensation reaction with *p*-amino-NN-diethylaniline sulphate (**I**) in an oxidising medium of $K_3Fe(CN)_6$. *Procedure*—To the ethanolic (96%) soln. containing, in 5 ml, salicylamide (**II**) (5 to 100 $\mu$g), phenyl salicylate (**III**) (10 to 200 $\mu$g) or methyl salicylate (**IV**) (10 to 200 $\mu$g) add $NaHCO_3$ soln. (5%) (2 ml) for **II**, or 0·05 *M* $Na_2B_4O_7.10H_2O$ - 0·1 *N* NaOH (1:1) (2 ml) for **III**, or 0·05 *M* $Na_2B_4O_7.10H_2O$ - 0·1 *N* NaOH (7:3) (2 ml) for **IV**, followed by a soln. of **I** (0·2% for **II**, or 1% for **III** or **IV**) (1 ml) and $K_3Fe(CN)_6$ soln. (2% for **II**, 10% for **III** or **IV**) (1 ml). Mix and add benzene (10·0 ml) and shake for $\simeq$ 30 sec. Dry the benzene layer with anhyd. $Na_2SO_4$ and measure the colour in a Pulfrich photometer (filter S61). The method was applied with good results to the determination of **II**, **III** and **IV** in pharmaceuticals. The mechanism of the reaction is discussed. J. ZÝKA

4948. **Circular paper chromatographic technique for the separation of mixtures of sulpha drugs.** Swarup Narain Tewari and Dharam Narain Tripathi (Clin. Lab., The Mall, Kanpur, India). *Z. anal. Chem.*, 1959, **166** (5), 356–357 (in English).—*Procedure*—One drop of the mixture (dissolved in aq. $NH_3$) is placed at the centre of a Whatman No. 1 filter-paper (18 cm diam.). The solvent-feeding wick is applied to the centre of the spot on the paper, which is placed on a Petri dish and covered with another dish. Acid (*n*-butanol - acetic acid - water, 5:1:4) and alkaline (*n*-butanol - conc. aq. $NH_3$, 5:1) solvents are used. After the development the disc is dried, and sprayed with a 1% soln. of *p*-dimethylaminobenzaldehyde in 3% HCl to give orange - yellow circular bands, which are compared with known chromatograms. $R_F$ values for 8 sulphonamides are listed for each solvent.
B. B. BAUMINGER

4949. **Simultaneous colorimetric determination of chloramphenicol cinnamate and sulphonamides.** G. Machek (Kontroll-Lab. der Biochem. G.m.b.H., Kundl, Tirol). *Sci. Pharm.*, 1959, **27** (1), 24–34.—To determine sulphonamides, diazotise the diluted sample, couple with N-1-naphthylethylenediamine and measure the extinction at 540 m$\mu$. To determine chloramphenicol cinnamate, reduce the diluted sample with alkaline sodium dithionite before application of the colorimetric method and use the coloured soln. from the first determination as the blank. The method has been applied to the assay of syrups and 'chartae' (*cf. Anal. Abstr.*, 1958, **5**, 4282). Results are accurate to within about $\pm$ 2%.
A. R. ROGERS

4950. **The dead-stop titration. V. Dead-stop titration, derivative polarographic titration, and potentiometric polarography of sulphanilamide derivatives by diazometry with two platinum electrodes.** Takehisa Enoki and Katsuaki Morisaka (Coll. of Pharm., Kitayashita, Minami-kawachi-gun, Osaka). *J. Pharm. Soc. Japan*, 1958, **78** (4), 432–435.—The dead-stop titration of aromatic amines making use of the redox reversible system with $HNO_2$ was studied with reference to the influence of temp. and the rate of titration. By the use of 0·1 *N* $NaNO_2$ in *N* $H_2SO_4$ at 0°, the change in current for dead-stop titration with a potential difference of 150 mV and that in potential for derivative polarographic titration (3 $\mu$A) are 5 $\mu$A and 50 mV, respectively, at the end-point, corresponding to an error of 5% for sulphanilamide and 3% for aniline. By the use of 0·5 *N* $NaNO_2$, the error is decreased to one fifth. Near the end-point, the rate of titration is decreased to 1 ml per min.
K. SAITO

4951. **Complexometric determination of some derivatives of phenothiazine. I. Determination of chlorpromazine.** L. Przyborowski and L. Krówczyński (Dept. of Pharm. Chem., Med. Acad., Lublin). *Chem. Anal., Warsaw*, 1959, **4** (1–2), 59–67.—The method consists in pptg. chlorpromazine (**I**) from soln. by means of an excess of a standard soln. of $CdI_2$, in the presence of KI or HI. A ppt. of the formula $(C_{17}H_{19}N_2SCl)_2.H_2CdI_4$ is formed, and the excess of $CdI_2$ in the filtrate is determined complexometrically, with Xylenol orange as indicator. The method is suitable for determining **I** as the pure substance and in pharmaceutical preparations (*e.g.*, tablets and injections); it takes only 30 min., and is satisfactorily accurate, despite a small loss of the determined substance.
W. B. MIASKOWSKI

4952. **Comparison of the methods for the determination of nikethamide.** Heng-Yun Yu and Duenn Tao (Anal. Dept., First Nat. Pharm. Plant, Shanghai). *Acta Pharm. Sinica*, 1959, **7** (3), 122–125.—The simple rapid method for the determination of nikethamide (*cf.* Fritz, *Brit. Abstr. C*, 1951, 49) is based on the non-aqueous titration in glacial acetic acid with $HClO_4$ soln. in glacial acetic acid, the end-point being detected potentiometrically, or visually by the use of crystal violet as indicator. *Procedure*—Weigh 0·2 g of sample into a 100-ml conical flask and dissolve in glacial acetic acid (5 ml) that has previously been adjusted to a bluish-green with $HClO_4$, with crystal violet as indicator. Add 0·5% crystal violet soln. (2 drops) and titrate with 0·1 *N* $HClO_4$ in glacial acetic acid to a bluish-green end-point. The proposed method gives a standard error of $\pm$ 0·056% and is more accurate than the hydrolysis or refractometric methods.
S. H. YUEN

4953. **Determination of diethylenediamine [piperazine].** J. Erben (State Inst. for Control of Drugs, Prague). *Československ. Farm.*, 1959, **8** (1), 18–19.—The method is based on the reaction of piperazine (**I**) with $HgCl_2$ soln. and on the complexometric determination of the excess of reagent after the removal of the ppt. *Procedure*—Dissolve **I** (0·1 g) in $H_2O$ (10 ml), add 0·1 *M* $HgCl_2$ (30·0 ml), heat the mixture slightly, then cool, and filter off and wash the ppt. with $H_2O$. To the filtrate add an excess of 0·05 *M* EDTA (disodium salt), then aq. $NH_3$ - $NH_4Cl$ buffer soln. (pH 10), dilute to 300 ml and titrate with 0·05 *M* $MgSO_4$, with Eriochrome black T (C.I. Mordant Black 11) as indicator.
J. ZÝKA

4954. **Polarographic behaviour of iodinated X-ray contrast agents in buffered media.** P. Kabasakalian and J. McGlotten (Schering Corp., Bloomfield, N.J., U.S.A.). *Anal. Chem.*, 1959, **31** (4, Part I), 513–516.—Ten X-ray contrast agents containing iodine were studied polarographically in 50% ethanol - water at various pH values between 1·3 and 10·5. The effects of temp., sample concn. and pH on the wave form and height were examined. All the compounds tested gave well-defined and reproducible polarograms at some pH in the system used, and the diffusion currents were linear with respect to concn. over a fairly wide range.
G. P. COOK

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*See also Abstracts*—**4819**, Determination of formaldehyde and paraformaldehyde. **4821**, Determination of formaldehyde in technical hexamine. **4827**, Titration of sulphonamides. **4892**, Isolation

of coumestrol and antibiotics. **4976**, Determination of thiamine. **4978**, Separation of pyridoxine and ascorbic acid. **5016**, Determination of halothane and chloroform vapour.

## Food

*Foods and food additives, beverages, edible oils and fats, vitamins.*

4955. **Simple method for determining the protein content of wheat and flour.** L. Feinstein and J. R. Hart (Biol. Sci. Branch, AMS, U.S. Dept. of Agric., Beltsville, Md., U.S.A.). *Cereal Chem.*, 1959, **36** (2), 191–193.—A rapid turbidimetric method, which gives reproducible results, is described. *Procedure*—Shake flour or ground wheat (1·0 g) with 100 ml of 0·05 *N* NaOH for 15 min., and centrifuge the suspension at 6000 r.p.m. for ≮ 10 min. Dilute a 5-ml aliquot of the clear supernatant liquid to 50 ml with aq. sulphosalicylic acid soln. (3%, w/v), mix thoroughly, and immediately measure the turbidity of a 4-cm layer in a photo-electric colorimeter with a 540-mμ filter against a blank of sulphosalicylic acid soln. Determine the protein by reference to a calibration curve. S. C. JOLLY

4956. **Polarographic determination of cystine in wheat and flour hydrolysates.** W. F. Daum, J. E. DeVries and B. S. Miller [Standard Oil Co. (Ind.), Neodesha, Kans., U.S.A.]. *Cereal Chem.*, 1959, **36** (2), 176–185.—The cystine content of flour from 11 different varieties of wheat determined by this improved polarographic method agreed well with those determined by chemical and microbiological methods. *Procedure*—Heat ground wheat or flour (1·0 g) with 4·0 *N* HCl (25 ml) for 0·5 hr. at 15 lb pressure, cool rapidly, dilute the hydrolysate to 200 ml, and filter. Dilute a 3-ml aliquot of the filtered hydrolysate to 50 ml with electrolytic medium ($1{\cdot}6 \times 10^{-3}$ *M* $CoCl_2$, 0·105 *M* $NH_4Cl$ and 0·105 *M* aq. $NH_3$, prepared fresh each day from stock soln.), and record the polarogram within 5 min. of mixing. Measure the cystine wave-height as the difference in mm between the diffusion current of $Co^{3+}$ (obtained from the electrolytic medium with no added cystine) and the minimum of the catalytic wave due to cystine (Wostmann, *Ibid.*, 1950, **27**, 391). Prepare a standard curve by adding increments (2·0 to $12{\cdot}0 \times 10^{-2}$ mg) of cystine to 3-ml aliquots of the filtered hydrolysate (in which the cystine has been destroyed by treatment with 10 ml of 1% $H_2O_2$ for 17 hr. at 18° to 40°, and decomposing the excess of $H_2O_2$ by heating on a steam bath for 30 min.), diluting to 50 ml with electrolytic medium, and recording the polarogram. S. C. JOLLY

4957. **Variations in the gross composition of milk as related to the breed of the cow: a review and critical evaluation of the literature of the United States and Canada.** T. V. Armstrong (Ohio State Univ., Columbus, U.S.A.). *J. Dairy Sci.*, 1959, **42** (1), 1–19.—A review is presented, with 53 references. W. H. C. SHAW

4958. **Determination of degradation products of ascorbic acid [in milk].** J. Tobias and E. O. Herreid (Illinois Univ., Urbana, U.S.A.). *J. Dairy Sci.*, 1959, **42** (3), 428–440.—The method described is based on reaction with 2:4-dinitrophenylhydrazine for the determination of ascorbic acid, dehydroascorbic acid ("total" ascorbic acid) and 2:3-dioxo-L-gulonic acid (**I**). **I** is then determined separately after treatment with thiourea and $H_2S$. Results are compared with those obtained by the 2:6-dichlorophenolindophenol method. Small amounts of **I** were found in raw milk (1 to 2 days old), but little or none in dried skim or evaporated milk. The **I** content of pasteurised milk, initially low, increased considerably on storage at 40° F. W. H. C. SHAW

4959. **Application of the chemical inhibition method for vitamin D to evaporated milk.** S. W. Jones, W. W. Morris and J. B. Wilkie (Div. Nutrition, Food and Drug Admin., Dept. of Health, Education and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1959, **42** (1), 180–186.—The method used for pharmaceutical preparations (*cf.* Wilkie *et al.*, *Anal. Abstr.*, 1959, **6**, 1538) is modified. Fat is extracted before saponification; for this purpose two extractions with diethyl ether suffice. After saponification it is necessary to employ two columns of MgO - Hyflo Supercel, followed by one of $Al_2O_3$. In the $Al_2O_3$ column the carotene is eluted with 1 ml of diethyl ether and then with 6 ml of light petroleum. The $SbCl_3$ reagent is used to give a colour complex, which is measured at 500 mμ, contributory colour produced by vitamin-A decomposition products being allowed for by employing acetic anhydride to inhibit the formation of that due to vitamin D. A. A. ELDRIDGE

4960. **Analysis of milk for rotenoids.** M. Jacobson, I. Hornstein and R. T. Murphy (Entomol. Res. Div., Agric. Res. Service, U.S. Dept. Agric., Beltsville, Md., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1959, **42** (1), 174–176.—Rotenoids in milk, resulting from the use of sprays containing rotenone on cattle, may be detected by a spectrophotometric or a chromatographic method. The butter fat is extracted with a mixture of methyl cyanide and aq. $Na_2SO_4$ soln.; the soln. is washed with hexane and then extracted with $CHCl_3$, which is subsequently evaporated, and the residue is dissolved in $CCl_4$. The soln. is then chromatographed in a specially prepared alumina column, and eluate fractions are examined spectrophotometrically at 270 mμ. Alternatively, the $CCl_4$ is removed by evaporation and the residue, dissolved in acetone, is spotted on paper. Methanol - benzene - water (5:1:1) is used for development, followed by a $KMnO_4$ spray. The limits of sensitivity are 0·04 and 0·006 p.p.m., respectively, for rotenone and dehydrorotenone. [A. A. ELDRIDGE

4961. **Rapid spectrophotometric method for measuring cheese ripening.** D. G. Vakaleris and W. V. Price (Wisconsin Univ., Madison, U.S.A.). *J. Dairy Sci.*, 1959, **42** (2), 264–276.—The method is based on the u.v. absorption of a Na citrate - HCl extract of the sample; the extinction is almost entirely due to water-soluble tyrosine and tryptophan, which are determined by a two-component analysis. Results on 40 samples of Cheddar cheese correlated well with the water-soluble N (Kjeldahl method) and with organoleptic assessment of the degree of ripening. *Procedure*—Homogenise mechanically 10 g of cheese with 40 ml of 0·5 *M* Na citrate soln. and 80 ml of water. Transfer quant. to a 200-ml flask and dilute to volume. To 100 ml of liquid add 10 ml of 1·41 *N* HCl and dilute to 125 ml. The pH value should be 4·4 ± 0·05. Filter through a Whatman No. 42 paper, dilute an aliquot of the clear filtrate with an equal volume of water and measure the extinction (E) at 274 to 275 mμ (max.) against a blank prepared

from 20 ml of 0·5 *M* Na citrate, 10 ml of 1·41 *N* HCl and 220 ml of water. The coeff. of correlation of E with water-soluble N is 0·958. For the separate determination of tyrosine (*A*) and tryptophan (*B*) as moles per litre of the spectrophotometric soln., measure the extinctions at 270 mμ and 290 mμ; then $A = (0{\cdot}95E_{270} - 1{\cdot}31E_{290}) \times 10^{-3}$ and $B = (0{\cdot}307\ E_{290} - 0{\cdot}020 \times E_{270}) \times 10^{-3}$. Correlation coeff. with water-soluble N are 0·964 and 0·886, respectively. W. H. C. SHAW

4962. **New method of assay of foodstuff dyes. Use of quaternary ammonium salts.** B. Drevon and J. Laur (Lab. d'Intendance des Subsistances, Fac. de Méd. et de Pharm., Lyon, France). *Ann. Falsif.*, 1959, **52**, 155–161.—The dyes are extracted from foodstuffs by combination with a quaternary ammonium salt and extraction with $CHCl_3$ (Auerbach reaction), then separated by chromatography and determined colorimetrically. *Procedure*—The sample is dissolved or suspended in water (proteins are digested with pepsin) and an amount containing 5 to 10 μg of dye is adjusted to pH 9 with $Na_2CO_3$. Chloroform (10 ml) is added, and, if after stirring for 10 min. it becomes coloured, any basic dyestuffs are determined in it; if it remains colourless it is rejected. The aq. soln. and any ppt. are treated with a large excess of cetyl*cyclo*hexyldimethylammonium bromide, and shaken with $CHCl_3$ for 10 min., and the extraction is repeated until the aq. layer is colourless. The $CHCl_3$ soln. are evaporated at low temp. The residue is dissolved in 0·5 ml of $CHCl_3$ and transferred to bands of Arches 302 paper impregnated with alumina (preparation described), and a chromatogram is run with *n*-butanol - ethanol - water - 20% aq. $NH_3$ (10:5:5:2). The dyes are identified by their $R_F$ values and estimated by cutting out each spot, eluting with 20% aq. $NH_3$ and determining the dye photometrically.
E. J. H. BIRCH

4963. **Analysis of synthetic food colours prescribed in India.** B. R. Roy, A. R. Sundararajan and S. N. Mitra (Central Food Lab., Calcutta). *J. Sci. Ind. Res., India, C*, 1959, **18** (2), 38–40.—A scheme of analysis is given to serve as a routine procedure for the separation, detection, identification and determination of 11 synthetic water-soluble food colours prescribed by the Indian Government. The conventional wool-dyeing test and the colour reactions of the dyed wool and aq. extracts of the colours are used for detection and identification. The identification is confirmed by paper chromatography. The determination is carried out by chromatographing soln. of the dyes in water or *n*-butanol on Whatman No. 1 paper, eluting the chromatogram with 50% aq. ethanol and measuring the eluate in a Beckman spectrophotometer. I. JONES

4964. **Use of a new development chamber for paper-chromatographic detection of subsidiary constituents of colouring matters for foods.** J. Eisenbrand and B. Koether (Chem. Untersuchungsamt f. das Saarland, Saarbrücken, Germany). *Z. Lebensmitt Untersuch.*, 1959, **109** (3), 218–222.—A description is given of the Koether chamber in which 40 parallel runs can be developed with an ascending solvent on a spirally folded sheet. Most of the substances examined contain subsidiary related colouring matters and substances detectable under u.v. light. During exposure of the chromatograms to daylight for 7 days, some of the previously visible subsidiary spots disappear and are sometimes replaced by u.v. fluorescent spots; fluorescent spots may also appear in new positions.
P. S. ARUP

4965. **Note on the paper chromatography of oil-soluble food colours.** E. Mark and G. G. McKeown (Food and Drug Lab., Dept. of Nat. Health and Welfare, Ottawa, Canada). *J. Ass. Off. Agric. Chem.*, 1959, **42** (1), 213–214.—By means of the procedure of reversed phase chromatography described, quant. separations of a prepared mixture containing Yellow AB (C.I. Solvent Yellow 5), Yellow OB (C.I. Solvent Yellow 6), Orange SS (C.I. Acid Orange 20) and Oil red XO (C.I. Solvent Orange 7) were achieved. The loaded paper was developed with aq. acetone, and the ethanolic eluates of the separated zones were examined spectrophotometrically. A. A. ELDRIDGE

4966. **Artificial food colours. I. Characters and properties of permitted water-soluble food colours.** R. Garcia Olmedo and L. Villanúa (Dept. of Food Res., Madrid Univ.). *An. Bromatologia*, 1959, **11** (1), 9–47.—A classification scheme for dyes based on that of Rota is presented in extended tabular form, and the 25 water-soluble colours permitted by Spanish food law are located in the scheme. Data on chemical and physical properties, standards of purity, applications and toxicology are presented for each colour.

**II. Spectrophotometry of the water-soluble colours.** A. Carballido and L. Villanúa. *Ibid.*, 1959, **11** (1), 49–108.—Absorption curves are reproduced for the 25 water-soluble food colours permitted in Spain, which include Acid yellow G (C.I. Acid Yellow 9); tartrazine; quinoline yellow; Sunset yellow FCF (C.I. Food Yellow 3); carmoisine; amaranth; Ponceau 4R (C.I. Food Red 7); Erythrosine BS (C.I. Food Red 14); indigo carmine; auramine; Rhodamine B (C.I. Food Red 15); brilliant croceine; methyl violet; acid violet (C.I. Food Violet 1); Acrilan violet S4BN (C.I. Food Violet 2) and brilliant green. Graphs of curves grouped according to colour, chemical function, class in Rota's classification and chemical class show that spectrophotometric identification is possible for yellow, violet or green permitted colours, while for other colours spectrophotometric data can assist in the interpretation of the results obtained from chemical and chromatographic methods.

**III. Spectrophotometry of red, orange and yellow water-soluble colours at controlled pH.** A. Carballido and L. Villanúa. *Ibid.*, 1959, **11** (1), 109–178.—Absorption curves for 17 colours, including Acid yellow G; tartrazine; auramine; quinoline yellow; Sunset yellow FCF; carmoisine; amaranth; Ponceau 4R; Erythrosine BS; Rhodamine B and brilliant croceine, at controlled pH values ranging from 1 to 11, are presented, and their application to the identification of food colours is discussed. E. C. APLING

4967. **Determination of sorbic acid. I.** W. Diemair and K. Franzen (Univ. Inst. f. Lebensmittelchem., Frankfurt a.M.). *Z. anal. Chem.*, 1959, **166** (4), 246–253.—Sorbic acid may be detected by paper chromatography in 1:3:3-trimethyl-2-methyleneindoline and the zone rendered visible by spraying with methyl *p*-hydroxybenzoate. The procedure is unsuited to quant. work because of the poor contrast between the sorbic acid zone and the general background. For quant. work it is recommended that the sample be steam-distilled

and the extinction of the distillate determined at 256 mμ (pH 5·9) or 262 mμ (pH 4·0). Results are quoted for several proprietary beverages.

**II.** W. Diemair and K. Franzen. *Ibid.*, 1959, **166** (5), 325–333.—Sorbic acid anhydride, formed by boiling the acid with acetic anhydride, reacts with 2-(methylthio)benzothiazolium ethyltoluene-*p*-sulphonate (**I**) to give a green dye. *Procedure*—Sorbic acid (3 to 5 mg, or the equiv. of sodium or calcium salt) is placed in a flask (500 to 750 ml) containing 100 g of $MgSO_4.7H_2O$, and 100 ml of $H_2O$ and 4 ml of HCl (25%) are added; 90 to 100 ml of the soln. is distilled. The distillate is filtered if necessary, 2 to 3 drops of HCl are added and the soln. is shaken with diethyl ether (5 × 20 ml). The ether is dried with 5 g of $P_2O_5$ for 5 to 10 min., immersing the flask in ice-water, then evaporated and the residue kept in a desiccator for 1 hr. The dry residue is dissolved in 5 ml of acetic anhydride and filtered. An aliquot of the filtrate (1 ml) is added to a mixture of dry **I** (30 mg) and anhyd. Na acetate (50 mg) and the mixture is immersed in an oil bath at 135° for 15 min. The soln. is diluted with methanol to 11 ml, shaken, and cooled, and the colour is measured after 15 min. at 652 mμ, with 0·25-cm cells. T. R. Andrew
B. B. Bauminger

4968. **Pesticides in food products. V. Determination of hydrocyanic acid in food products by oscillographic polarography.** V. Jedlička and A. Pašek (Centr. Res. Inst. of Food Ind., Prague). *Československ. Farm.*, 1959, **8** (3), 138–142.—Hydrocyanic acid in *M* $NH_4Cl$ as supporting electrolyte yields a sharp incision on the cathodic axis of the curve of the function $dV/dt = f(V)$ which can be used for detection; its depth can be used for the quant. determination of the amount of HCN present (> 100 μg per ml) after a preliminary distillation. The reliability of the method was tested by analysing various food products (*e.g.*, milk, vegetables and juices), blood and urine. J. Zýka

4969. **Pre-determination of the albumin stability of beer with 2:6-dichlorophenolindophenol.** K. Silbereisen and G. Wittmann (Inst. f. Gärungsgewerbe, Berlin). *Brauerei, Wiss. Beil.*, 1959, **12** (3), 47–51.—The use of 2:6-dichlorophenolindophenol (**I**) as a precipitant in the rapid predetermination of the albumin stability of beer has been exhaustively studied. Twenty-eight beers were tested under standard conditions. To each sample was added 0·01 *N* aq. **I** in the proportion of 3 ml of reagent to 97 ml of beer. The mixtures were maintained at 20° for 24 hr. and after a further 24 hr. the turbidities were measured in a nephelometer. Results were compared with values obtained by normal air oxidation; beers from the same brewery showed good agreement. Values given by the ammonium sulphate and Esbach precipitation methods were also compared with those from air oxidation. Neither of these methods is suitable for the pre-determination of albumin stability. In another series of experiments beers were oxidised to various degrees with air, and then tested for albumin stability with **I**. The results indicate that the test gives a satisfactory indication of the probable stability. S. M. Marsh

4970. **Gravimetric bromimetric determination of iodine value and some quantitative determinations of substitution with a flat weighing glass.** W. Heidbrink (Gödecke & Co. A.-G. Chem. Fabrik, Berlin). *Fette, Seif., Anstrichmitt.*, 1959, **61** (3), 194–199.—The flat weighing glass consists of a pair of glass plates between which a viscous sample can be pressed into a film. The plates are separated when the sample is being dried or exposed to a gas, and closed for weighing. Apparatus for producing a bromine atmosphere and a procedure for the determination of moisture and of unsaturation in the same sample are described. In sunlight, Br-substitution reactions can be carried out in the same apparatus and their course followed by the increase in wt. G. Burger

4971. **Determination of epoxides in oils and fats.** L. Krull (Margarine Union A.-G., Hamburg-Bahrenfeld). *Fette, Seif., Anstrichmitt.*, 1959, **61** (3), 223–227.—The effect of other oxidation products on the determination of epoxides in fats has been examined and an argentimetric method is proposed which is less susceptible to interference than other methods studied. A soln. of the sample in *iso*propyl alcohol is boiled under reflux with an excess of collidine hydrochloride and the excess of $Cl^-$ is titrated with $AgNO_3$, with Congo red as indicator. The thermal stability of epoxides and the effect of epoxides on the determination of characteristic values of fats were also studied. The epoxide group is stable up to 150°. The carbonyl value and the hydroxyl value are affected, and the peroxide value is not affected, by the presence of epoxides. G. Burger

4972. **Determination of *iso*oleic acids in fats.** J. Pokorný and B. Kakáč (Sch. of Chem. Technol., Prague). *Průmysl Potravin*, 1959, **10** (1), 19–20.—The determination of *iso*oleic acids by the lead salt method yields results that are lower by 1 to 9% than those obtained with the use of the spectrometric method. J. Zýka

4973. **Determination of the yield of oil in winterisation pastes.** G. B. Martinenghi (Studio di Ric. Chim. per Olii, Milan). *Olii Min.*, 1959, **38** (2), 37–40.—Pastes obtained in removing solid fat from olive oils contain ≃70 to 80% of oil. The sample (20 g) is dissolved in hexane (100 ml) cooled to −20°, kept for 4 to 5 min. and then filtered at this temp. The amount of oil in the filtrate is determined by removing the solvent and drying to constant wt. at 110° to 120°. For pastes with different oil contents the conditions are slightly modified. An additional washing with the solvent will give a figure higher by ≃5%, but the value obtained without this treatment is considered to represent the practical oil yield. L. A. O'Neill

4974. **Separation of lipids by gas - liquid chromatography.** S. R. Lipsky, R. A. Landowne and J. E. Lovelock (Dept. of Internal Med., Yale Univ. Sch. of Med., New Haven, Conn, U.S.A.). *Anal. Chem.*, 1959, **31** (5), 852–856.—By the use of high-efficiency capillary columns in conjunction with the ionisation detection system of Lovelock (*cf. Anal. Abstr.*, 1958, **5**, 3208), the analysis of complex mixtures of the esters of long-chain saturated and unsaturated acids in quantities < 0·1 μg has been achieved. Thus, methyl oleate and methyl elaidate were easily separated on a column (200 ft. × 0·01 in. inside diam.) coated with Apiezon L and operated at 207° with an inlet pressure of 40 p.s.i. of argon. A. R. Rogers

4975. **Identification of position isomers of some stearic acid derivatives by infra-red spectroscopy. Study of *trans*-6- through -11-octadecenoic acids and corresponding contiguously substituted dihydroxystearic acids in the crystalline state.** Heino

Susi (Agric. Res. Service, U.S. Dept. of Agric., Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 910–913.—The absorption spectra of the *trans*-mono-unsaturated fatty acids show a progression of equally spaced strong bands between 1180 $cm^{-1}$ and 1350 $cm^{-1}$. The number of bands is related to the length of the chain segment next to the carboxyl group and can be used to determine the position of the double bond. The corresponding dihydroxy acids can be distinguished by their spectra in the 800 $cm^{-1}$ to 1200- $cm^{-1}$ region. G. BURGER

4976. **Coulometric micro-determination of thiamine hydrochloride.** K. Kalinowski and Z. Sykulska (Dept. of Pharm. Chem., Med. Acad., Lódź). *Acta Polon. Pharm.*, 1959, **16** (2), 111–114.—Thiamine was determined quant. by means of electrolytically generated iodine in an alkaline medium by using the dead-stop method with two platinum electrodes in a specially constructed cell. *Procedure*—To the anode compartment of the cell add 10 ml of the test soln. and 3 ml of 0·1 *N* NaOH. After 5 min. add 10 ml of 10% KI soln. To the cathode compartment add 10 ml of water then equal quantities of the soln. as added to the anode compartment. Cool the cell and its contents to 0° to 2°, switch on the mixing device, then the indicating circuit and finally the generating circuit and record the time from this point. Continue the electrolysis till the presence of free iodine is indicated. Then carry out a blank determination with 10 ml of water instead of the test soln. Calculate the amount of the vitamin in mg from the equation given. One molecule of thiamine reacts with one atom of iodine. The accuracy is ± 0·5% for 3 to 9 mg of thiamine hydrochloride. The method can be applied to the determination of thiamine in tablets and capsules. W. ROUBO

4977. **The determination of total riboflavine content in cereals and cereal products.** J. Janicki and E. Kaminski (Inst. f. Landwirtschaftl. Technol., Landwirtschaftl. Hochsch., Poznan, Poland). *Getreide u. Mehl*, 1959, **9** (1), 9–12; (2), 18–21.—Riboflavine was determined in wheat by the fluorescence and lumiflavin methods. By varying the conditions of extraction, riboflavine values from 2·27 to 14·40 μg per g (fluorescence method) and 1·35 to 7·14 μg per g (lumiflavin method) were obtained. The pH of the soln. was found to affect the fluorescence intensity. In both methods, concentration and $CHCl_3$ washing of the extract affected the final results. After the preliminary autolysis, hydrolysis with NaOH instead of $H_2SO_4$ reduces the recovery. Better results are obtained with a concn. of 2% of original substance than with 5%. In the lumiflavin method, the extraction of the photolysed material with $CHCl_3$ should be continued until the $CHCl_3$ extracts show no fluorescence. It is shown that the photolysis of riboflavine produces lumichrome as well as lumiflavin. The possibility of the formation of lumichrome from riboflavine by the action of micro-organisms present in grain, and of interference in the fluorescence method by xanthopterins, is discussed.
J. V. RUSSO

4978. **Ion exchangers in pharmaceutical analysis. XII. Separation of pyridoxine and ascorbic acid.** A. Jindra (Dept. Biochem., Charles' Univ., Prague). *Československ. Farm.*, 1959, **8** (1), 15–16.—The separation is carried out with the use of a combination of ion exchangers of different basic strengths. *Procedure*—Place a 3-ml column of a weak basic anion exchanger (Amberlite IR-4b) over a column of strong basic anion exchanger (Amberlite IRA-401) and add a mixture of pyridoxine hydrochloride (2 to 3 mg) and ascorbic acid (20 mg) (20 to 30 drops per min.). Wash the columns with $H_2O$ (50 ml), remove the upper column, elute the pyridoxine retained on the lower column with 0·1 *N* HCl (25 ml) and determine photometrically with diethyl-*p*-phenylenediamine (*cf.* Hrdý and Urbanová, *Anal. Abstr.*, 1958, **5**, 2374). J. ZÝKA

4979. **Influence of surface-active compounds on the polarographic determination of L-ascorbic acid.** J. Davídek and J. Manoušková (Centr. Res. Inst. of Food Ind., Prague). *Prûmysl Potravin*, 1959, **10** (2), 96–98.—The presence of 1·25% of gelatin and 10% of dextran or soluble starch makes the measurement of the polarographic wave of ascorbic acid slow. To prevent this difficulty and the low results caused by surface-active compounds, a method is recommended, in which, for the evaluation of results by the method of standard addition, a soln. of ascorbic acid with added surface-active compound is used. With this modification the polarographic method yields results which are in agreement with those by the titrimetric procedure.
J. ZÝKA

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*See also Abstracts*—**4722**, Determination of N. **4761**, Determination of F in foods. **4826**, Identification of organic acids from alcoholic fermentations. **4927**, Detection of alkaloids in foods.

## Sanitation

*Analysis of air, water, sewage, industrial wastes, industrial poisons.*

4980. **Special indicator tubes for a rapid determination of nitrogen oxides in the air of industrial establishments.** L. A. Mokhov, Yu. F. Udalov and V. S. Khalturin. *Zhur. Prikl. Khim.*, 1959, **32** (2), 452–453.—The construction of special indicator tubes, 80 to 100 mm in length and 3 to 5 mm in diam., is described. Add a saturated ethanolic soln. of H-acid (8-amino-1-naphthol-3:6-disulphonic acid) (20 ml) to silica gel (1 g). Mix for 2 min., evaporate off the ethanol, add a 0·5% ethanolic soln. of *p*-aminobenzoic acid (20 ml), dry again, mix with a 0·1% ethanolic soln. of $NiCl_2$ and grind the indicator mass before drying it to a suitable consistency. Introduce the indicator gel into the indicator tubes to make a 2-mm layer. Above this layer introduce a 2-mm layer of silica gel followed by a glass- or cotton-wool plug and seal the open, broad end of the tube. *Procedure for the determination of nitrogen oxides*—Break open the tube at both ends and pass 100 ml of the test air through the broad end of the tube so that it emerges from the cone-shaped end. Compare the colour of the indicator with a standard colorimetric scale. In the presence of nitrogen oxides the indicator changes from pale pink to a crimson-brown. The indicator is sensitive to 0·0005 mg per litre. K. R. C.

4981. **Infra-red spectral detection of carboxylic acids and aldehydes in air-borne particulates.** E. Sawicki and T. R. Hauser (U.S. Dept. of Health, Educ. and Welfare, Cincinnati, Ohio). *Anal. Chem.*, 1959, **31** (4, Part I), 523–527.—The reactions of various types of carbonyl compounds with $PCl_5$ and diethylamine were investigated. In all cases

the carboxylic acid C=O band moves towards a shorter wavelength on reaction with $PCl_5$ and towards a longer wavelength on reaction with diethylamine. Aldehydes lose their C=O band and 2-carboxydiarylketonic compounds lose their ketone group on reaction with $PCl_5$. All other types of carbonyl compounds tested show only minor changes in the 5·5 to 6·5-$\mu$ region. The application of these studies to air-borne particulates has shown that carboxylic acids can be identified in the benzene-soluble fraction and in the acid sub-fraction. Data for about 40 compounds are listed.
G. P. Cook

4982. **Micro-determination of dissolved oxygen by hypodermic syringe.** P. Holland (Power Station, Poole, Dorset, England). *Chem. & Ind.*, 1959, (7), 218–219.—Less than 0·01 p.p.m. of dissolved O in boiler-feed water can be determined rapidly and accurately by the apparatus and procedure described. To the sample collected (through a probe) in a bottle with a "Suba-Seal" cap are added the following reagents in succession—(*i*) 40% NaOH soln. (0·05 ml), (*ii*) 40% $MnSO_4$ soln. (0·05 ml), and (*iii*) conc. HCl satd. with *o*-tolidine (0·1 ml). The injections are made with an all-glass syringe (1 ml, graduated to 0·1 ml) and stainless-steel needle. The colour developed is compared in an absorptiometer, preferably with that given by similarly treated samples of de-aerated water containing known amounts of satd. soln. of O. Ionised interfering substances and insol. compounds should be removed on a mixed-bed resin column, but un-ionised reducing substances react too slowly to cause interference. Reproducibility is at least as good as the sensitivity of *o*-tolidine (0·003 p.p.m.); a reagent blank is necessary for samples containing O in excess of 0·02 p.p.m. W. J. Baker

4983. **Portable analyser for determination of dissolved oxygen in water. Application of rapid-dropping mercury electrode.** C. P. Tyler and J. H. Karchmer (Humble Oil & Refining Co., Baytown, Tex.). *Anal. Chem.*, 1959, **31** (4, Part I), 499–502.—By using a horizontal dropping mercury electrode with a short drop-time (0·2 to 0·33 sec.) a current is produced which is relatively insensitive to agitation or to sample-flow. The sample flows by gravity through a cell containing the horizontal cathode and a mercury pool anode. A voltage of $-1{\cdot}6$ V *vs.* the mercury pool is applied; the circuit includes a microammeter (which also serves as a voltmeter) and a variable resistance. The total current is corrected for temp. and residual current (found by de-aerating a fresh sample and again recording the current); 0·1 p.p.m. of O can be determined in $H_2O$ (pH 4·5 to 11); if the salt concn. in the sample is $> 0{\cdot}05$ or $< 0{\cdot}001$ *M*, 2 ml of reagent (5 g of gelatin, 2 g of phenol and 0·3 g of NaCl in 100 ml of $H_2O$) is added to each 100 ml of sample. For calibration, a sample of $H_2O$ containing the reagent is aerated for 1 hr. and used 0·5 hr. later; it contains 8·10 p.p.m. of O at 26°.
P. D. Parr-Richard

4984. **Polarographic determination of dissolved oxygen. Study of drop time with rapid-dropping mercury electrode.** J. H. Karchmer (Humble Oil & Refining Co., Baytown, Tex.). *Anal. Chem.*, 1959, **31** (4, Part I), 502–508.—The rapid-dropping mercury electrode is suitable for continuously flowing streams and for amperometric titrations with continuous stirring. The effect of drop-time (*t*) and stirring on the diffusion current of O in water is discussed; a single capillary electrode mounted vertically, then horizontally, and finally scratched at the orifice and mounted vertically, was used for the tests. For the same flow-rate of mercury, *t* was 0·8 to 4 sec., 0·2 to 1·0 sec., and 0·025 to 0·07 sec., respectively. For very small drop-times, the current does not obey the Ilkovič equation; stirring affects the current less as *t* decreases and the rate of mercury-flow increases. When *t* is $< 0{\cdot}2$ sec. and the salt concn. is high, an anomalous current is produced. Simple equations relating *t* and mercury flow-rate can be used for the selection of suitable capillaries. P. D. Parr-Richard

4985. **Polarographic determination of oxygen. Anomalous current encountered with rapid-dropping mercury electrode.** J. H. Karchmer (Humble Oil & Refining Co., Baytown, Tex.). *Anal. Chem.*, 1959, **31** (4, Part I), 509–513.—In the determination of O in water an anomalous high current is obtained when the salt concn. is $> 0{\cdot}05\ N$; the effect is accentuated as the drop-time of the mercury decreases and the total current increases, and is related to the "water current." For the horizontal capillary used, the addition of 0·075% by wt. of gelatin suppressed the effect completely, giving curves similar to those found with drop-times of 3 to 6 sec., or in the absence of high salt concn.
P. D. Parr-Richard

4986. **B.D.H. indigo carmine method for determining dissolved oxygen in boiler feed water.** British Drug Houses, Ltd. *Chem. Age*, 1959, **81**, 618.—A simple colour-comparison method for the determination of $\geq 0{\cdot}12$ ml of O per litre is described. The reagents required are indigo carmine - glucose tablets, KOH soln. (51·5 g in $H_2O$ to make 100 ml) and glycerol. A modified Nessler cylinder (containing a reagent tube sealed with a glass ball) is filled with the sample, stoppered and inverted, so that the reagent flows into the water. The colour is compared with a standard disc in a Lovibond Nessleriser. Nickel, $Cu^{II}$ or Zn (1 p.p.m.), $Fe^{III}$ (3 p.p.m.) and small amounts of $SO_3^{2-}$ or hydrazine do not interfere. Hydrazine can be caused to react with *p*-dimethylaminobenzaldehyde to give a red or yellow colour in conc. or dil. soln., respectively, which can be determined spectrophotometrically (*cf.* Watt and Chrisp, *Brit. Abstr. C*, 1953, 161); urea and semicarbazide do not interfere. P. D. Parr-Richard

4987. **Determination of calcium, magnesium and total hardness by automatic spectrophotometric titration.** H. V. Malmstadt and T. P. Hadjiioannou (Univ. Illinois, Urbana, U.S.A.). *J. Amer. Wat. Wks Ass.*, 1959, **51** (3), 411–417.—Calcium is determined in the presence of Mg at pH 13, with Calcon (C.I. Mordant Black 17) as indicator. The total amount of Ca and Mg is determined at pH 10 with Eriochrome black T (C.I. Mordant Black 11) as indicator. Both titrations are automatically terminated at their end-points. Interference by heavy metals is prevented by adding a few drops of KCN soln. The results from more than 1000 samples with total hardness from 0·5 to 600 p.p.m. were reproducible and accurate. The automatic titration takes from a few seconds to a few minutes, according to the hardness. O. M. Whitton

4988. **Ion exchange - spectrographic determination of arsenic and phosphorus in river water.** R. Ko (General Electric Co., Hanford River Products Operation, Richland, Wash.). *U.S. Atomic Energy Comm.*, Rep. HW-59008, 1959, 14 pp.—Concn. as low as 0·001 p.p.m. were determined with a

precision of ± 0·001 p.p.m. (95% confidence level for a single measurement). One litre of sample was concentrated by anion exchange. Arsenic and P were eluted with *M* $HNO_3$ and determined in the eluate by d.c. arc excitation, with V as the internal standard. NUCL. SCI. ABSTR.

4989. **Separation and determination of microgram quantities of molybdenum in natural waters.** Ken Sugawara, Motoharu Tanaka and Shiro Okabe (Chem. Inst., Fac. of Sci., Nagoya Univ., Chikusa-ku, Nagoya). *Bull. Chem. Soc. Japan*, 1959, **32** (3), 221–222 (in English).—The Mo is first co-pptd. with either hydrated manganese oxide or ferric hydroxide, and then extracted with *n*-butanol - $CHCl_3$ as the thiocyanate and subjected to spectrophotometry at 475 mμ. The pH of the soln. is adjusted to 3·8 to ensure quant. co-pptn. of Mo and to give nearly 100% recovery. Co-pptn. with manganese oxide is preferred to co-pptn. with ferric hydroxide since the ppt. is quickly and easily filtered off and is more readily soluble in dil. HCl containing a small amount of $H_2O_2$. The optimum pH range for quant. pptn. is also wider. I. JONES

4990. **Analysis of strongly mineralised waters.** R. Marcille. *Chim. Anal.*, 1959, **41** (3), 105–109.—Waters from dry regions may change in composition during transit owing to bacterial action; thus, $SO_4^{2-}$ form $S^{2-}$, and $NO_3^-$ form $NH_4^+$. Sample bottles and corks must be clean and the addition of $CHCl_3$ (5 ml per litre) is recommended as a preservative. The determination of dry residue, alkalinity, $NO_3^-$ and $K^+$ is discussed. On heating the dry residue to 250° to dehydrate $CaSO_4.2H_2O$, some $Cl^-$ are lost if $MgCl_2$ is present, though $Ca(HCO_3)_2$ helps to prevent this. Such residues re-hydrate very rapidly. Alkalinity must be determined on the natural water, not on the dry residue, and contamination by gas heating must be avoided when $SO_4^{2-}$ are to be determined. For the determination of $K^+$ as $KClO_4$, excess of $HClO_4$ must be present during the evaporation, and the ethanol (satd. with $ClO_4^-$) must be acid (2 ml of $HClO_4$ per litre). A second evaporation is recommended to convert all NaCl into $NaClO_4$. The classical method of grouping elements in the dry residue by combining results for $CO_2$, $SO_4^{2-}$, $Cl^-$ and $NO_3^-$ with those for $Ca^{2+}$, $Mg^{2+}$, $K^+$ and $Na^+$ is recommended, and examples are given.
P. D. PARR-RICHARD

4991. **Application of an automatic titrator to sewage analysis.** J. C. Crowther (Houldsworth Sch. of Appl. Sci., Univ., Leeds, England). *Chem. & Ind.*, 1959, (10), 327–328.—Automatic potentiometric titrations of $NH_3$ and "oxidised N" can be completed in < 1 min. by connecting two titration units with one titrator by means of a change-over switch; the end-point is taken at pH 4·70. The burette tip is placed so that stirring carries the titrant towards the indicator electrode; the automatic change-over from fast to slow delivery can be adjusted to occur a few drops before the end-point. The apparatus consists of a Pye Universal pH meter, a Pye automatic titrator, and a switching unit. P. D. PARR-RICHARD

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*See also Abstracts*—**4758**, Determination of F in air. **4761**, Determination of F in water. **4875**, Determination of Tl in air. **5008**, Determination of demeton in air. **5073**, Alarm for detection of toxic gases.

## Agricultural analysis

*Soil, fertilisers, herbicides, pesticides, animal feeding-stuffs.*

4992. **Rapid determination of readily soluble magnesium in soils.** B. E. Beater and R. R. Maud (Sugar Expt. Station, Mount Edgecombe, Natal, S. Africa). *Chemist Analyst*, 1959, **48** (1), 10–11.—The colour produced by an acid extract of soil with Brilliant yellow (C.I. Direct Yellow 4) is measured absorptiometrically and compared with standards. *Reagent*—Dissolve 0·01 g of Brilliant yellow in 50 ml of methanol. Mix 30 g of 12% poly(vinyl alcohol) soln. with 50 ml of water, and add it with stirring to 900 ml of satd. lime water. Add the Brilliant yellow soln., stir and bottle. *Procedure*—Shake 2·5 g of soil (air-dry, 2 mm mesh) with 25 ml of 0·05 *N* $H_2SO_4$ for 1 min. Filter through an asbestos pad between two filter-papers with suction. To 1 ml of filtrate add 25 ml of reagent with rotation, set aside for 20 min. and measure the extinction with a green filter (560 mμ). Compare the result with those for standards obtained by adding 1 drop of 0·08% aq. $Al_2(SO_4)_3.18H_2O$ soln. to 1 ml of suitably diluted Mg soln. (3·058 g of $MgSO_4.7H_2O$ made up to 1 litre with 0·05 *N* $H_2SO_4$) and treating as described above. When the soil contains enough extractable Al to cause cloudiness, treat 5 ml of soil extract with 6 drops of 10% aq. $(NH_4)_2SO_4$ soln. and 5 ml of satd. lime water, set aside for 10 min., filter, and treat 2 ml of the filtrate as described above. The results are sufficiently close to those by titrimetric and flame-photometric methods to render the method suitable for agricultural advisory purposes. The acid extract of the soil can be used for flame-photometric determinations of Ca and K. R. E. ESSERY

4993. **Rapid method for the determination of total sulphur in soils and plants.** B. Butters and E. M. Chenery (Dept. of Agric., Kawanda Res. Sta., P.O. Box 265, Kampala, Uganda). *Analyst*, 1959, **84**, 239–245.—The method is turbidimetric. Standard soln. are prepared from an aq. soln. of $MgSO_4.7H_2O$ (50 μg of S per ml) acidified with acetic acid, 25% $HNO_3$ and $H_3PO_4$. Barium chloride crystals are added to each soln. and, after a specified number of inversions at specified time intervals, clear acacia gum soln. is added, the liquid is adjusted to a known vol., inverted again according to a specified procedure and its extinction is measured in a Spekker absorptiometer at 490 mμ. The calibration graph is linear. The soil sample is evaporated in an electric oven at 70° with 2 ml of $Mg(NO_3)_2$ soln., prepared from Specpure magnesium dissolved in $HNO_3$ (25 g in 500 ml), the residue is heated overnight in a stainless-steel oven at 300° and then digested with $HNO_3$ on a water bath. The cooled digest is adjusted to a known vol. and filtered. An aliquot is treated with 50% acetic acid and $H_3PO_4$ and the turbidity is developed as with the standard soln. A slightly modified procedure is used with plant material. The same batch of $BaCl_2$ crystals should be used for samples and standards, a reagent blank is necessary and determinations should be made in duplicate as occasional determinations may be in error by > 10%. A. O. JONES

4994. **Spectrophotometric detection of dicyandiamide in calcium cyanamide and in soil.** A. Pawlik (Stuttgart-Hohenheim, Inst. f. Pflanzenschutz d. Landwirtschaftl. Hochsch. Hohenheim). *Naturwissenschaften*, 1959, **46** (6), 203.—The u.v.

absorption spectrum of dicyandiamide shows a maximum at 215 mμ which can be used for the detection of dicyandiamide in aq. extracts from soil and calcium cyanamide in the presence of guanidine, dicyandiamidine and urea, and for its determination within 12% at a concn. of 5 mg in 100 g of soil. Nitrates interfere. G. BURGER

4995. **Composition and manurial value of poultry excreta, straw-droppings composts and deep litter. I. Introduction: experimental materials, methods of sampling and analysis.** J. Tinsley and T. Z. Nowakowski (Dept. of Soil Sci., Univ. of Aberdeen). *J. Sci. Food Agric.*, 1959, **10** (3), 145–150.—Evaluation of various manures has been made by determining their N, P and K contents; precautions were taken against loss of N as $NH_3$. A fresh weighed sample (20 to 30 g) is blended with $H_2O$ and the suspension inverted rapidly over a metal funnel divider to give four 100-ml fractions, which are then weighed. Total N is determined on one fraction, after reduction with 1 g of Devarda's alloy and 10 ml of 40% NaOH soln. (an acid-soaked plug preventing loss of $NH_3$), by Kjeldahl digestion with $H_2SO_4$; $NH_3$ is distilled and titrated in the usual way. To another fraction is added 0·1 *N* $H_2SO_4$ (25 ml) and $H_2O$ to make 250 ml; after setting aside overnight, soluble N is determined on the filtrate. Total soluble N is found by reduction and digestion as before, soluble N excluding $NO_3^-$ by adding $FeSO_4$ and conc. $H_2SO_4$ to destroy $NO_3^-$ before digestion, and $NH_3$ by distillation at pH 9. Soluble organic N and $NO_3^-$ are found by difference. Uric acid is determined by extraction with $Li_2CO_3$ and titration in LiCl - HCl soln. with $Ce(SO_4)_2.2(NH_4)_2SO_4$ soln. (*Analyst*, 1957, **82**, 110). The moisture of fresh samples is found by heating at 105° for 24 hr., and the pH after soaking a fresh sample for 1 hr. in $H_2O$. The ash content is measured by charring 5 g of dry material and heating overnight at 500°; the C (%) is taken to be 58% of the organic matter lost on ignition. After wet-ashing 1 g of dry material with $HNO_3$ - $HClO_4$, P in the diluted digest is determined by the molybdovanadophosphate method (Hanson, *J. Sci. Food Agric.*, 1950, **1**, 172). For K, 1 g of dry sample is moistened with $H_2SO_4$, ashed at 500° to 520° and extracted with dil. HCl; K is measured by flame photometry. Experimental errors are discussed and the precision is shown to be good. P. D. PARR-RICHARD

4996. **Improved microbiological method for nitrate determination [in forages].** R. M. Hill, H. Pivnick, W. E. Engelhard and M. Bogard (Dept. of Biochem. and Nutrition and Dept. of Bact., Univ. of Nebraska, Lincoln, U.S.A.). *J. Agric. Food Chem.*, 1959, **7** (4), 261–264.—The combined enzymatic and colorimetric method developed by Nason and Evans for the determination of $NO_3^-$ in plant materials (*J. Biol. Chem.*, 1953, **202**, 655) and modified by Garner *et al.* (*Anal. Chem.*, 1956, **28**, 1589) has been further improved by the use of a micro-organism (*Pseudomonas oleovorans* ATCC No. 8062) which does not produce nitrite reductase and does not have a nutritional requirement for $NO_3^-$. The maintenance of the stock culture and its preparation for the assay are therefore simplified, and the incubation time in the assay is less critical. Very good precision is attainable, and in most cases the results compare favourably with those obtained by a modified Devarda method. S. C. JOLLY

4997. **Simplified determination of molybdenum in plant material by 4-methyl-1:2-dimercaptobenzene (dithiol).** J. B. Bingley (Div. of Animal Health and Production, C.S.I.R.O., Parkville, Victoria, Australia). *J. Agric. Food Chem.*, 1959, **7** (4), 269–270.—A rapid, sensitive and accurate colorimetric method is described, capable of determining 0·1 to 5·0 μg of Mo in plant material without preliminary separation. The presence of sufficient Fe is essential for max. colour development, but Cu in the amounts usually present in plant material (> 30 μg per g) does not interfere. *Procedure*—Wet-oxidise the sample (1 g) with $H_2SO_4$, $HNO_3$ and $HClO_4$, evaporate the soln. twice to fuming, cool, dilute with 4 to 5 ml of water and boil vigorously for 15 sec. Add 0·25 ml of Fe soln. [9·1 g of $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$ in 100 ml of 2% $H_2SO_4$], dilute to 25 ml with water, add 0·25 ml of KI soln. (50% w/v), swirl occasionally during 10 min., discharge the iodine colour with $Na_2S_2O_3$ soln. (10% w/v), and add 0·25 ml of tartaric acid soln. (50% w/v) and 2 ml of dithiol reagent (dissolve 1 g in 500 ml of 1% NaOH soln. warmed to 38°, and add thioglycollic acid until a faint turbidity persists; store in a refrigerator and use within 1 month). Shake vigorously for 30 sec. and, after 30 min., add 5·0 ml of *iso*amyl acetate (boiling-range 136° to 142°) and again shake vigorously for 30 sec. Centrifuge the organic layer to remove water droplets, measure the extinction of the soln. at 680 mμ, and determine the amount of Mo by reference to a calibration curve prepared by treating similarly a standard soln. of Mo (prepared from molybdenum metal to contain 1 μg per ml). S. C. JOLLY

4998. **Colorimetric determination of 3:5-dinitrobenzamide in feeds by the Janovsky reaction.** H. F. Beckman and J. De Mottier (State Chem. Lab., Texas Agric. Exp. Sta., College Station, U.S.A.). *J. Agric. Food Chem.*, 1959, **7** (4), 280–282.—The Janovsky reaction for dinitro compounds has been adapted to the rapid routine determination of microgram amounts of 3:5-dinitrobenzamide (**I**) in poultry feeding-stuffs. The source of the feeding-stuff had little effect on recoveries of **I** (97·4 to 103·5% for 12 different materials), and 4-hydroxy-3-nitrophenylarsonic acid, NN′-di-(*m*-nitrobenzenesulphonyl)ethylenediamine, $N^4$-acetyl-$N^1$-(*p*-nitrophenyl)sulphanilamide and nitrophenide [di-(3-nitrophenyl) disulphide] did not interfere. *Procedure*—To 2·0 g of the feeding-stuff (containing 0·025% of **I**) in a 100-ml flask add anhyd. methanol to the mark, shake for 30 min. and filter. Evaporate a 20-ml aliquot to dryness, dissolve the residue in 10 ml of warm acetone, and rinse the vessel with 5 ml of conc. aq. $NH_3$, followed by 10 ml of acetone. Dilute the combined acetone soln. and rinsings to 25 ml with acetone, mix well, and after 45 min. in the dark measure the extinction at 580 mμ. For feeding-stuffs containing higher percentages of **I**, suitably dilute the methanolic extract so that a 20-ml aliquot contains 120 μg of **I**. Prepare a standard curve by adding 5 ml of conc. aq $NH_3$ to 20-ml aliquots of acetone soln. containing 0 to 10 μg of **I** per ml, and measuring the extinction as for the test soln. S. C. JOLLY

4999. **Determination of arsenic in some insecticides.** D. Pirtea and E. Antonescu (Chem. Res. Centre, Acad. R.P.R., Bucharest). *Acad. R.P.R., Stud. Cercet. Chem.*, 1959, **6** (3), 445–453.—The method is based on the reduction of the arsenic

compound to $AsH_3$, followed by oxidation to arsenate with $H_2O_2$ in the presence of KOH and titration of the As iodimetrically. H. SHER

5000. **Determination of HCH [hexachlorocyclohexane] and DDT in commercial preparations.** F. Strache (Hyg. Inst., Hamburg). *Fette, Seif., Anstrichmitt.*, 1959, **61** (3), 186–187.—On saponification with ethanolamine, HCH yields three $Cl^-$ per mol. and DDT yields one $Cl^-$. With metallic Na in *iso*propyl alcohol all five $Cl^-$ are split from DDT, and, similarly, all six $Cl^-$ are split off from HCH. Thus two $Cl^-$ determinations (by addition of an excess of standard $AgNO_3$ soln. and back-titration of the filtrate) measure the DDT and HCH separately. The reaction with ethanolamine is carried out in 2-ethoxyethanol soln. on a water bath. The reaction with Na is carried out by boiling the soln. in *iso*propyl alcohol with Na for 30 to 40 min. under reflux. G. BURGER

5001. **Gas chromatography of pesticides.** D. M. Coulson, L. A. Cavanagh and J. Stuart (Dept. of Chem., Stanford Res. Inst., Menlo Park, Calif., U.S.A.). *J. Agric. Food Chem.*, 1959, **7** (4), 250–251.—Lindane, parathion, aldrin and *pp'*-DDT were recovered quantitatively, with no evidence of decomposition, after passage through a gas-chromatographic column at 220° to 280° with He as the carrier gas, followed by absorption in $CS_2$ and subjection to i.r. analysis. Dieldrin, malathion and demeton can also be separated from pesticide mixtures. Toxaphene and chlordane gave complex chromatograms indicative of a mixture of components. The technique should be useful for the 'clean-up' and separation of pesticides in vegetable extracts. S. C. JOLLY

5002. **A fly bio-assay for the determination of organic phosphate pesticides.** D. F. McCaulley and J. W. Cook (Div. Food, Food and Drug Admin., Dept. of Health, Education and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1959, **42** (1), 200–207.—The method is described, and tabulated data show the effect of parathion, parathion-methyl, EPN (O-ethyl O-*p*-nitrophenyl phenylphosphonothioate), malathion, Systox, diazinon, Guthion [OO-dimethyl S-(4-oxo-3H-1:2:3-benzotriazine-3-methyl) phosphorodithioate], Trithion [S-(*p*-chlorophenylthio)methyl OO-diethyl phosphorodithioate] and Phosdrin (1-methoxycarbonyl-1-propen-2-yl dimethyl phosphate, 60% technical) individually on house-fly mortality and on the *in vivo* inhibition of fly cholinesterase. A close relationship is indicated. Lindane, DDT, isodrin and toxaphene showed no effect on cholinesterase. A. A. ELDRIDGE

5003. **Comparison of four cholinesterase methods of analysis for organic phosphate pesticides.** G. Yip and J. W. Cook (Div. Food, Food and Drug Admin., Dept. of Health, Education and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1959, **42** (1), 194–197.—The inhibition of cholinesterase was measured by the electrometric, titrimetric, manometric and colorimetric methods, with Systox as inhibitor. For 50% inhibition there was a maximum difference of ± 15% between the results, which are illustrated graphically. It was observed that the technical Systox employed became more potent with lapse of time. A. A. ELDRIDGE

5004. **Direct colorimetric analysis of cholinesterase-inhibiting insecticides with indophenyl acetate.** T. E. Archer and G. Zweig (Pesticide Residue Res. Lab., Univ. of California, Davis, U.S.A.). *J. Agric. Food Chem.*, 1959, **7** (3), 178–181.—Residues of the anticholinesterase insecticides, Sevin (1-naphthyl methylcarbamate), Thimet [OO-diethyl S-(ethylthio)methyl phosphorodithioate], Guthion [OO-dimethyl S-(4-oxo-3H-1:2:3-benzotriazine-3-methyl) phosphorodithioate] and Trithion [S-(*p*-chlorophenylthio)methyl OO-diethyl phosphorodithioate] are determined colorimetrically by measuring the product of the hydrolysis of indophenyl acetate at pH 8·0 by the surviving enzyme. The effects of source of enzyme, enzyme concn., temp. and pre-incubation time are recorded. Crystalline bovine erythrocyte acetylcholinesterase was a satisfactory source of enzyme; enzymes from human and horse sera were relatively insensitive to Sevin, to which bee-brain cholinesterase, on the other hand, was particularly sensitive. Results by this colorimetric method agreed well with those obtained potentiometrically and by paper chromatography. M. D. ANDERSON

5005. **Cholinesterase-inhibition method of analysis for organic phosphate pesticides: effect of enzyme-inhibitor reaction time upon inhibition.** E. D. Nesheim and J. W. Cook (Div. Food, Food and Drug Admin., Dept. of Health, Education and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1959, **42** (1), 187–193.—The phosphorylation or inhibition of the enzyme was followed by time studies in order to ascertain the optimum degree of enzyme phosphorylation within a reasonable and practicable incubation time. The rate of formation of the enzyme - phosphoryl complex, its stability, and the reactivation, if any, of the enzyme, are involved. Studies on the effect of time of incubation of Phosdrin (1-methoxycarbonylprop-1-en-2-yl dimethyl phosphate, 60% technical) or Systox [mixture of OO-diethyl S (and O)-2-(ethylthio)ethyl phosphorothioate] or of oxidised diazinon, malathion, EPN (O-ethyl O-*p*-nitrophenyl phenylphosphonothioate), parathion-methyl and parathion with human plasma cholinesterase show that the cholinesterase is sensitive to different quantities of the various pesticides and that the rates of reaction vary considerably. Incubation for 30 min. is recommended. A. A. ELDRIDGE

5006. **Detection of phosphorothioic acid esters.** R. Fischer and N. Otterbeck (Inst. f. Pharmakog. d. Univ. Graz). *Sci. Pharm.*, 1959, **27** (1), 1–6.—Develop an extract of the sample, or alternatively a sulphur-containing saponification product, with either acetone - $H_2O$ - 12% aq. $NH_3$ (130:61:9) or methanol - $H_2O$ - 1% aq. $NH_3$ (19:1:1) by the method of "test-tube chromatography" (Fischer and Otterbeck, *Ibid.*, 1957, **25**, 242). Momentarily dip the chromatogram in a soln. containing sodium azide and iodine. Sulphur-containing compounds are revealed as colourless spots on a brown background. The sensitivity is 1 or 2 μg. Values of $R_F$ are tabulated for parathion, diazinon, Chlorthion [O-(3-chloro-4-nitrophenyl) OO-dimethyl phosphorothioate], malathion, metaSystox (demeton-methyl) and thiometon (OO-dimethyl S-ethylthioethyl phosphorothiolothionate) and their saponification products. A. R. ROGERS

5007. **Extraction and identification of parathion and diazinon from lettuce.** R. E. Moddes and J. W. Cook (Div. Food, Food and Drug Admin.,

Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1959, **42** (1), 208–211.—The use of methyl cyanide for extraction of the pesticides is recommended. The extract is diluted with water and the pesticide transferred to pentane. Interfering plant extractives are removed on a column of $Al_2O_3$ followed by one of MgO - Celite. The pesticide is finally separated by paper chromatography, with 4% of mineral oil in diethyl ether as the stationary phase and aq. ethanol as the mobile phase, the paper being then exposed to an atmosphere of Br in $CCl_4$ and sprayed with fluorescein soln. Recoveries of parathion and diazinon of 92 to 107% are reported. A. A. ELDRIDGE

5008. **Identification of Systox [demeton]. Use of sampling-tube techniques in toxicological chemistry.** K. Grosskopf. *ChemikerZtg*, 1959, **83** (4), 115–117.—The use of small sampling tubes containing adsorbent for the detection and determination of toxic gases is outlined and their advantages are considered. A procedure of this type has been developed for the detection and semi-quant. determination of demeton, which is based on the addition reaction of the thioether sulphur with $AuCl_3$, the product being developed with an aq. soln. of chloramine T to give a highly coloured complex. The sampling tube (illustrated) contains a carrier impregnated with $AuCl_3$, and above this is an ampoule containing the developing reagent. A measured quantity of air is drawn through the tube by means of a gas-detection pump and the ampoule is then broken at a marked point so that the developing soln. wets the carrier. The appearance of a red - orange ring on the adsorbent indicates the presence of demeton. The method is sensitive to 1 $\mu$g, and by taking a sample of 2 litres of air it is possible to detect a concn. of 0·5 mg per cu. metre. The amount of demeton can be estimated approx. by comparing the length of the coloured ring with a series of standard tubes prepared from soln. containing known amounts of demeton. The method may also be applied to the determination of demeton in organic materials by drawing a pentane extract of the material (*e.g.*, leaves sprayed with insecticide) through the tube. Typical results are tabulated. S. M. MARSH

5009. **Photofluorimetric method for determination of Co-Ral [O-(3-chloro-4-methylumbelliferone) OO-diethyl phosphorothioate] [Bayer 21/199] residues in animal tissues.** C. A. Anderson, J. M. Adams and D. MacDougall (Chemagro Corp., Kansas City, Mo., U.S.A.). *J. Agric. Food Chem.*, 1959, **7** (4), 256–259.—A highly sensitive method is described for the determination of traces ($\simeq$ 0·02 p.p.m.) of this pesticide and/or its oxygen analogue in a variety of animal tissues. Extracts of the tissues (50 g) are purified by solvent extraction and chromatography, and the pesticide is then hydrolysed to a more highly fluorescent decomposition product (3-chloro-4-methyl-7-hydroxycoumarin). The fluorescence of the soln. is measured at 410 m$\mu$ after activation at a wavelength of 330 m$\mu$. With $>$ 0·1 p.p.m. of pesticide, the average deviation from the mean was $\simeq$ 10%; with higher concn. the precision was slightly better. S. C. JOLLY

5010. **Paper-chromatographic identification of antu [1-(1-naphthyl)-2-thiourea].** K. Fischer. *Arch. Kriminol.*, 1957, **120** (3–4), 72–73.—Antu can be isolated in the acid ether extract of the classical Stas-Otto procedure. The ether is evaporated to dryness and the residue is dissolved in methanol. The soln. is spotted on S. & S. No. 2043 filter-paper. This paper is then prepared for overnight ascending chromatography with ethanol - amyl alcohol - aq. $NH_3$ (2:2:1). After air-drying the paper it is sprayed with a saturated soln. of Br in 10% NaOH. Pure antu gives a violet spot at $R_F$ 0·79. As little as 30 $\mu$g can be identified. CHEM. ABSTR.

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*See also Abstracts*—**4908**, Determination of organic acids in grass. **4960**, Rotenoids in milk.

## 5.—GENERAL TECHNIQUE AND APPARATUS

### General

5011. **New type of semi-automatic pipette.** I. Heyduk (VŽKG, Ostrava, Czechoslovakia). *Chem. Průmysl*, 1959, **9** (4), 196–197.—The sample is sucked by means of a water-pump into the pipette, the manipulation of the three-way tap of which permits the filling of the pipette and the measurement of the vol. The arrangement is suitable for measuring toxic soln. J. ZÝKA

5012. **Improvements in or relating to pipettes.** M. C. Sanz. Brit. Pat. 815,199, date appl. 21.6.57. Date appl. Switzerland 10.9.56; date appl. U.S.A. 11.4.57.—A capillary tube having a passage capable of retaining a predetermined vol. of liquid by capillary action extends into a chamber which has its lower portion in communication with a vessel containing a reserve of the liquid. Means are provided (*e.g.*, by compressing the vessel, which is made of deformable plastic) for causing the liquid in the reserve vessel to rise into the chamber and submerge the adjacent end of the tube whereby the capillary passage is filled with liquid. The capillary tube may be of polyethylene to facilitate calibration by cutting off the end until the predetermined vol. is contained between the meniscusses. J. M. JACOBS

5013. **A simple reservoir burette for alkaline solutions.** H. F. Holden (Walter and Eliza Hall Inst. Med. Res., Melbourne, Australia). *Aust. J. Exp. Biol. Med. Sci.*, 1959, **37** (1), 107–108.—A simple and cheap reservoir burette that protects $Ba(OH)_2$ soln. from atmospheric $CO_2$ is described and illustrated. N. E.

5014. **A recording titrator.** R. C. Williams, R. S. Ruffin and L. A. Mounter (Dept. of Biophys., Med. Coll. of Virginia, Richmond, U.S.A.). *Anal. Chem.*, 1959, **31** (4, Part I), 611–615.—The instrument described has been designed for the titration of acidic and basic groups liberated in hydrolytic enzyme reactions. It is simple, rugged, compact and accurate, and needs no external accessories apart from a water bath for temp. control. The instrument can be used with small samples and is completely free from drift. K. A. PROCTOR

5015. **Apparatus for titrations using ultra-violet light.** D. H. Wilkins (Res. Lab., General Electric Co., Schenectady, N.Y., U.S.A.). *Talanta*, 1959, **2** (1), 88–89.—The apparatus is a wooden box painted dull black inside and containing three 8-W fluorescent lamps (General Electric F8T5B1B). A burette passes through the top of the box and a

viewing slot is provided in the side. The contents of the titration vessel are stirred by a magnetic stirrer inside the box. W. T. CARTER

5016. **Acoustic gas analyser.** L. Molyneux (Dept. of Anaesthetics, Univ. of Durham, England). *J. Sci. Instrum.*, 1959, **36** (3), 118–120.—The concn. of halothane ($CF_3CHBrCl$) or $CHCl_3$ vapour (0 to 4%) in a mixture with air and oxygen is measured with an accuracy of $\pm$ 0·25% by comparing the velocity of sound in the mixture before and after removal of the vapour with activated charcoal. An all-transistor electronic circuit is described. G. SKIRROW

5017. **Improved method and apparatus for determining and controlling the moisture content of dielectric materials [particularly textile fibres].** Commonwealth Sci. and Indust. Res. Organisation. Brit. Pat. 815,000, date appl. 30.8.56; date appl. Australia 31.8.55.—The material is located between the plates of a test condenser into which voltages of different frequencies are fed simultaneously. The resulting voltage changes, which are dependent on the moisture content of the material, are converted into logarithmic voltages. These logarithmic voltages are subtracted to obtain a voltage which is a function of the ratio of the change in voltage drops across the plates of the test condenser, corresponding to each feed frequency when the material is placed between the plates. J. M. JACOBS

5018. **Apparatus for the accurate determination of oxygen in a small sample of gas.** J. Muzyczuk (Dept. Phys.-Chem. Anal., Inst. Mining Res., Mikołów, Poland). *Chem. Anal., Warsaw*, 1959, **4** (1–2), 365–372.—A glass apparatus is described and illustrated for the determination of the O content of a 10-ml sample of air or other gas, in the range up to >20% (v/v), with an accuracy of $\pm$0·02%. The reduction in pressure caused by the reaction of phosphorus with O is allowed to suck water from a micro-burette, and the percentage of O is calculated from the vol. of water displaced. The manipulation and maintenance are simple and the reaction time is $\gtrsim$ 8 min. Data are provided for the calibration of the burette and the calculation of corrections, which are usually small. W. B. MIASKOWSKI

5019. **Simple expedient for evaporating small amounts of solvent.** R. L. Clements (Dept. of Plant Biochem., Univ. of California, Riverside, U.S.A.). *Chemist Analyst*, 1959, **48** (1), 20.—The solvent (3 to 10 ml) is contained in a vial closed with a neoprene stopper carrying a glass tube. The tube is connected to the vacuum line by a length of Tygon tubing (0·25 in. outside diam.), by means of which the vial is suspended from a clamp in a 250-ml beaker, preferably of plastic or lined with some resilient material, which is placed on a magnetic stirrer, and is filled with water at a suitable temperature. When the stirrer is started and the vacuum applied, the vial is swirled at a frequency depending on the length of tubing between the clamp and the vial, the best position being found by experiment. By this means, 5 ml of light petroleum in a 7·5-ml vial can be evaporated in 2 min. at 30°. The apparatus is illustrated. R. E. ESSERY

5020. **Useful fraction collector for small-scale vacuum distillations.** D. W. S. Evans (Univ., Nottingham, England). *Chem. & Ind.*, 1959, (7), 219–220.—The glass apparatus described and illustrated is a modification of the Kon rectangle and will give a clean separation of 2 to 3 ml of distillate. Advantages claimed are (*i*) all traces of a fraction can be removed from the run-off tube before connecting a second receiver, (*ii*) this receiver can then be evacuated without affecting the distillation, and (*iii*) only two simple double-oblique-bore stopcocks are required. W. J. BAKER

5021. **Simple micro-Kjeldahl apparatus.** Taiichi Asami (406th Med. Gen. Lab., Camp Zama, Japan). *Anal. Chem.*, 1959, **31** (4, Part I), 630.—With the steam-distillation apparatus described and illustrated, alkali was never distilled over on strong heating unless foam reached the outlet to the condenser. If foam was produced it tended to be destroyed before reaching the outlet. G. P. COOK

5022. **Vacuum sublimation device for the separation and purification of small quantities of substances.** G. Schmidt (Inst. f. gerichtl. Med., Univ., Erlangen, Germany). *Mikrochim. Acta*, 1959, (3), 406–418.—The apparatus described and illustrated is based on the principle of temperature gradients (*cf.* Askew *et al.*, *Proc. Roy. Soc., B*, 1930, **107**, 748; Behrens and Fischer, *Naturwissenschaften*, 1954, **41**, 13). It is possible to carry out in a single operation the continuous fractionation of several substances which have different sublimation behaviours. With the size of apparatus chosen ($\simeq$ 45 cm long $\times$ 5 cm diam.) amounts of substance from a few $\mu$g to $\simeq$ 30 mg may be handled. As the various concentric tubes are transparent it is possible to follow the course of the sublimation. By the use of a removable plastic film for the deposition of the sublimate, the fractions may be recovered without alteration of their crystalline state. D. F. PHILLIPS

5023. **Expedient for micro-filtration.** J. M. Corliss (U.S. Army Chem. Warfare Lab., Army Chem. Center, Md.). *Chemist Analyst*, 1959, **48** (1), 16.—A 2-ml hypodermic syringe is inserted, by means of a 22-gauge hypodermic needle, into the rubber stopper connecting the siphon tube and filter-tube of the apparatus of Niederl and Niederl. A variable air-space is thus introduced into the system and, by manipulation of the plunger, particles can be dislodged from the walls of the pressure tube, attainment of solubility equilibria is hastened so that volumes of wash-liquor can be controlled, and clogged filter-tubes can be freed. A diagram is given. R. E. ESSERY

## Chromatography, ion exchange, electrophoresis

5024. **Apparatus for chromatography permitting concentration of the constituents.** R. Audran and G. Reutenauer (Lab. Kodak-Pathés, Vincennes, France). *Bull. Soc. Chim. France*, 1959, **26** (1), 46–51.—An apparatus is described consisting of a base plate cooled with water and carrying a circular trough, and a central polished portion acting as a reflector to a small heating spiral. A cone made from a 145° sector of a circular paper (9·5 cm diam.) is placed with its edge in the trough and point upwards, and the assembly is covered with a glass cone which can be closed by a tap or connected to a vacuum pump. As the solutes ascend the paper with the solvent they are separated partly by

chromatography and partly by crystallisation owing to evaporation of the solvent and are concentrated by this evaporation and by the narrowing arc of paper. The evaporation is promoted by the heater. By an adaptation replacing the heating spiral by an insulated lead, separation by electrophoresis can be effected. Examples of organic and inorganic separations are given. E. J. H. BIRCH

5025. **Variable gradient device for chromatography.** E. A. Peterson and H. A. Sober (Lab. of Biochem., U.S. Dept. of Health, Education and Welfare, Bethesda, Md.). *Anal. Chem.*, 1959, **31** (5), 857–862.—In this device, for which constructional details are given, small changes in specific portions of the elution gradient are possible without any physical change in the apparatus. Exact duplication of data can be obtained.
K. A. PROCTOR

5026. **Improved method of heating chromatographic columns.** L. R. Bunney, R. Phillips and E. C. Freiling (U.S. Naval Radiolog. Defense Lab., San Francisco, Calif.). *Anal. Chem.*, 1959, **31** (5), 968.—In the method described, a heating jacket of electrically conducting Pyrex-glass tubing is used. The electrically conductive film is on the outside of the tubing and is chemically inert, very hard and transparent. The max. operating temp. is 350°. K. A. PROCTOR

5027. **Centrifugal force in paper chromatography and electrophoresis.** H. J. McDonald, L. P. Ribeiro and L. J. Banaszak (Loyola Univ., Chicago, Ill., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 825–829.—A simple and effective apparatus is described for the application of centrifugal force to paper chromatography and ionography on paper discs rotating in a horizontal plane. The patterns are similar to those obtained under the usual conditions, but the development time is markedly reduced. Centrifugal and electrical forces may be applied independently, in sequence or simultaneously.
K. A. PROCTOR

5028. **Some artefacts in paper chromatography.** G. Zweig (Univ. of California, Davis, U.S.A). *Anal. Chem.*, 1959, **31** (5), 821–824.—Artefact spots have been observed on paper chromatograms of amino acids, organic acids and bases, and inorganic ions. Some are due to esterification by, or complex formation with, the solvent system; others are due to multiple ionic species and geometrical isomers. Corrective measures are recommended to minimise their occurrence. A. R. ROGERS

5029. **Quantitative evaluation of chromatograms by double decomposition with simple radioactive reagents. I. The use of $Ag^{131}I$ in radiometric estimation of organic and phosphoric acids.** Z. J. Zubrzycki, A. Z. Budzyński and I. G. Campbell (Dept. of Radiobiol. and Radiochem., Inst. of Nuclear Res., Warsaw, Poland). *Talanta*, 1959, **2** (2), 165–170.—The chromatograms of fatty acids (lauric, myristic, palmitic and stearic), of phosphates (ortho-, pyro-, trimeta- and hypo-phosphates) and of glucose 1-phosphate are obtained by specified procedures and air-dried. They are then hung in a special vessel made of paraffin wax, and treated by immersion with satd. aq. Ag acetate soln. for 15 min. After being washed with water (3 × 5 ml), they are treated by immersion for 15 min. with 0·01 *M* aq. KI containing 3 $\mu$C of $K^{131}I$ per ml, then washed thrice with water as above, and allowed to dry in the dark at room temp. Activity measurements are made in a previously described instrument (Budzyński *et al.*, "Second U.N. Int. Conference on Peaceful Uses of Atomic Energy," P/1588, Geneva, 1958), with a slit width of 2 mm. The integrated activities of the spots are linearly related to spot content, and the maximum (peak) spot activity is proportional to the log. of spot content for fatty acids and phosphates, but not for glucose 1-phosphate. Errors are as follows for the loads stated—fatty acids, 4·6 to 7·1% (50 to 400 $\mu$g); phosphates, 4·9 to 11·2% (50 to 500 $\mu$g); glucose 1-phosphate, 1·9% (20 to 300 $\mu$g).
R. E. ESSERY

5030. **Carrier displacement chromatography on ion-exchange resins.** D. L. Buchanan (Radioisotope Service, Veterans Admin. Hosp., West Haven, Conn., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 833–836.—Amino acids may be separated by differential migration into and through a zone of resin which has first been saturated with an appropriate acid or base. The method has been applied to the isolation of free amino acids from picric acid extracts of rat muscle. The capacity of a given column and the concn. of amino acid in the percolate are greater when the carrier is a weak base than when mineral acids or buffers are used.
A. R. ROGERS

5031. **Gas chromatography.** N. H. Ray (Plastics Division, I.C.I. Ltd., Welwyn Garden City, England). *J. Soc. Glass Tech.*, 1959, **43**, 100T–112T.—A review of methods and apparatus is given, with 25 references. J. A. SUGDEN

5032. **Fractional co-distillation in gas-chromatography apparatus.** G. H. Cady and D. P. Siegwarth (Dept. of Chem., Univ. of Washington, Seattle). *Anal. Chem.*, 1959, **31** (4, Part I), 618–620.—A method of separating small amounts of volatile substances is described, in which the separation is dependent upon liquid - vapour (or solid - vapour) equilibria, a temp. gradient in a packed column and a rising temp. in the column as a whole. The separated substances emerge in the order of decreasing volatility and substances may be separated which react with the type of packing usually used in gas chromatography. Substances which sublime may also be separated. K. A. PROCTOR

5033. **Analysis of aqueous mixtures by gas chromatography.** B. Smith (Inst. f. Organ. Kem., Chalmers Tekniska Högskola, Göteborg, Sweden). *Acta Chem. Scand.*, 1959, **13** (3), 480–488 (in English).—Examples are given illustrating the use of polyethylene glycol 200 and 400, glycerol, diglycerol, hexanetriol, triethanolamine, Tween 80 and glycerol mono-oleate as stationary phases for the analysis of aq. soln. of low-molecular-weight alcohols, aldehydes, ketones and carboxylic acids.
W. T. CARTER

5034. **Separations by continuous electrochromatography.** A. Karler (Karler Lab., Berkeley, Calif., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 848–851.—A general account of the principles and practice of continuous-flow curtain electrophoresis is given and illustrated by the purification of plague toxin and tetanus toxoid. D. G. MOSS

5035. **Starch electrophoresis. I. Starch block electrophoresis.** H. Bloemendal (Dept. of Biochem., Netherlands Cancer Inst., Amsterdam). *J. Chromatography*, 1959, **2** (2), 121–135.—A review is presented of apparatus, technique and applications, with 62 references. W. T. CARTER

5036. **Improved technique of agar-gel electrophoresis on microscope slides.** R. J. Wieme (Lab. of the Med. Clinic, Univ. of Ghent, Belgium). *Clin. Chim. Acta*, 1959, **4** (3), 317–321.—The electrophoresis tank has end vessels, with platinum electrodes filled with buffer soln., which communicate through large holes with inner vessels filled with buffered agar gel of the same composition as that used for coating the slides. The centre compartment of the tank is filled with light petroleum as cooling fluid. Samples (1 to 3 $\mu$l) are introduced into grooves cut in the gel on the slides, which are placed gel downwards so as to form a bridge between the agar blocks; a current of 25 to 35 mA is passed for 25 min. and, after drying, the slides are stained with Amido black 10B (C.I. Acid Black 1). By this technique a minimum of 9 fractions appears in normal human serum. H. F. W. KIRKPATRICK

5037. **Coloured substances as an experimental tool in the study of electrophoretic techniques.** H. Peeters and P. Vuylsteke (St. Jans Hosp., Bruges, Belgium). *Clin. Chim. Acta*, 1959, **4** (1), 58–61 (in English).—The investigation of conditions during electrophoresis with the help of dyes, to aid the development of techniques, is described. H. F. W. KIRKPATRICK

5038. **Electrophoresis tank suitable for wide application.** R. Frentz (Inst. de Biol., Fac. des Sci., Nancy, France). *Clin. Chim. Acta*, 1959, **4** (3), 340–345.—Details are given of the construction of a tank suitable for all types of electrophoresis. H. F. W. KIRKPATRICK

### Optical

5039. **Spectrochemical analysis with the help of spectra resolved in time by means of a rotating disc.** A. Bardócz and R. W. Tarbeling (Spectroscopic Dept., Cent. Phys. Res. Inst., Hungarian Acad. of Sci., Budapest). *Magyar Kém. Foly.*, 1959, **65** (3), 126–128.—At the beginning of spark discharges a strong background is observed in which the weaker lines tend to disappear, *i.e.*, the curves used in spectroscopy become too flat for evaluation. This initial background can be separated by using a rotating sector (which covers part of the length of the slit) and an electronically controlled spark generator, actuated by a photocell. This photocell receives its light from a source through a mirror fixed to the rotating axis of the sector. The amplifying circuit of the cell also includes a phase-shifting device so that the position of the sector with respect to the slit can be varied. The detection of Mn in aluminium at 2949 A is quoted as an example; this method increases the sensitivity by one order of magnitude. A. G. PETO

5040. **Induced-percussion electrode-packing machine.** A. Strasheim and E. J. Tappere (Nat. Phys. Res. Lab., Pretoria, S. Africa). *Appl. Spectroscopy*, 1958, **13** (1), 12–14.—With the machine described, more material can be packed into an electrode cavity than is possible by hand or with a vibrational-type machine. For some materials the reproducibility of the amount packed is better than $\pm$ 1%. K. A. PROCTOR

5041. **Test-tube adapter for Beckman DU spectrophotometer.** B. Zak and L. A. Williams (Wayne State Univ., Detroit, Mich., U.S.A.). *Chemist Analyst*, 1959, **48** (1), 17–18.—To facilitate the measurement of the colours of two immiscible layers, and render their separation unnecessary, a wooden cell-holder (illustrated) is constructed to fit the instrument. A pin passes transversely across the hollow in which the cell is inserted, at right angles to the light-path. When the pin is in position, it supports the cell so that the lower layer intercepts the light and can be read. When the pin is withdrawn, the cell drops on to a cork pad at the bottom of the hollow, and the upper layer can then be read. During extraction, centrifuging and reading, the cell is closed with a tightly fitting plastic stopper. R. E. ESSERY

5042. **Analytical possibilities of micro-wave spectroscopy.** L. Grifone (Ist. Chim. Fis., Univ. di Padova, Italy). *Ric. Sci.*, 1959, **29** (4), 706–723.—The advantages and disadvantages of the technique of micro-wave spectroscopy in analytical chemistry are discussed. It is suggested that a measuring apparatus incorporating some of the latest electronic devices (backward wave oscillator, highly sensitive crystals and memory tube) should be of value for qual. and quant. determinations. L. ZANONI

5043. **Infra-red cell assembly for volatile solids.** G. J. Janz and S. S. Danyluk (Dept. of Chem., Rensselaer Polytech. Inst., Troy, N.Y., U.S.A.). *Appl. Spectroscopy*, 1959, **13** (2), 48–49.—The simple and inexpensive cell described can be used for volatile solids when strictly anhydrous conditions and controlled atmospheres are essential. K. A. PROCTOR

5044. **Window materials for use in infra-red analyses involving nitrogen dioxide.** A. P. Altshuller and I. R. Cohen (Public Health Service, U.S. Dept. of Health, Education and Welfare, Cincinnati, Ohio). *Anal. Chem.*, 1959, **31** (4, Part I), 628–629.—The effects of 0·17% of nitrogen dioxide on calcium fluoride, barium fluoride and arsenic trisulphide are reported. Calcium fluoride windows appear to be completely satisfactory. K. A. PROCTOR

5045. **Levelling device for alkali halide pressed disc preparation.** H. W. Morgan (Oak Ridge National Lab., Tenn., U.S.A.). *Appl. Spectroscopy*, 1959, **13** (2), 48.—The device described can be used to ensure clear, reproducible discs up to 3 mm in thickness. The levelling of the powder can be carried out in about 30 sec. and the device is easily made from a 5-in. length of brass rod having a diameter $\simeq$0·005 in. smaller than the internal diameter of the die. K. A. PROCTOR

5046. **Halocarbon oil as a mulling medium for infra-red spectra.** D. S. Crocket and H. M. Haendler (Univ. of New Hampshire, Durham, U.S.A.). *Anal. Chem.*, 1959, **31** (4, Part I), 626–627.—Halocarbon oil (series 11–14) has a viscosity similar to that of Nujol, and is as easy to work with. It produces no interference in the region from 4000 to 1300 $cm^{-1}$ and has been used for both inorganic and organic compounds. K. A. PROCTOR

5047. **Electrostatic sample preparator for infra-red spectroscopy of powders.** H. F. Hazebroek (Koninkl. Shell-Lab., Amsterdam). *Spectrochim. Acta*, 1959, (1), 1–5.—Strongly coherent films of a selected particle size may be obtained by elutriation of powder samples with an inert gas, followed by electrostatic precipitation on to a suitable optical

collector. Details of the apparatus are given, and a typical spectrum, covering the 2·5 to 15-$\mu$ wavelength region, of a powdered quartz sample deposited on a rock-salt plate is compared with that of a similar sample dispersed in a potassium bromide pellet. P. T. BEALE

5048. **Report on first X-ray fluorescence round-robin test.** A.S.T.M. Task Group on X-ray Fluorescence Spectroscopy. *Appl. Spectroscopy*, 1959, **13** (1), 3–7.—Four factors affecting the precision of X-ray fluorescence spectroscopic methods were examined and gave the following results in terms of coeff. of variation—re-setting the operating conditions of the X-ray tube, $\pm$ 0·5%; re-positioning the X-ray spectrometer at the line peak, $\gtrsim \pm$ 0·5%; estimating composition, $\gtrsim \pm$ 10% of the amount present; precision of mixing powders to a nominal composition, $\pm$ 7%. The statistical nature of the X-ray process was found to agree experimentally with theory.
K. A. PROCTOR

5049. **A simple photometer.** B. Večerek and J. Večerková (Inst. Med. Chem., Charles' Univ., Prague). *Chem. Průmysl*, 1959, **9** (3), 137–138.—Details are given for the construction of a simple type of apparatus suitable for routine photometric analyses in the visible range. Ordinary galvanometers used with titrimetric apparatus are suitable for the indication of the light intensity. J. ZÝKA

5050. **Micro-photometer for colorimetric titrations.** A. Holasek, H. Lieb and K. Winsauer (Univ., Graz, Austria). *Mikrochim. Acta*, 1959, (3), 402–405.—The micro-photometer described is suitable for the exact detection of end-points when carrying out colorimetric or nephelometric titrations in vol. of 0·5 to 2·5 ml. Cylindrical cells enable a built-in magnetic stirrer to be used. D. F. PHILLIPS

5051. **Continuous colorimetric analyser and recorder for oxygen control in inert gases.** R. Šourek and A. Rečka (Dusíkárny n.p., Ostrava, Czechoslovakia). *Chem. Průmysl*, 1959, **9** (2), 71–75.—The apparatus described has been tested for controlling the content of O in nitrogen and in mixtures of nitrogen and oxygen used in the synthesis of $NH_3$, and in the production of A. The range is 0·002 to 0·03% (v/v), with an accuracy of 0·0005%. The determination is based on the absorption of O in an alkaline soln. of Na anthraquinone-2-sulphonate, the reduced form of which is red whereas the oxidised form is colourless. The apparatus differs from similar types in that the continuous replacement of the soln. is effected by means of a simple regulating device. J. ZÝKA

5052. **Colorimetric apparatus for gas testing. II. Apparatus for visual determination of oxygen.** J. Wacławik and S. Waszak (Anal. Dept., Inst. of Gen. Chem., Warsaw). *Chem. Anal., Warsaw*, 1959, **4** (1–2), 343–349.—The visual colorimetric determination of O in gases is based on the reaction of O with an alkaline soln. of Na anthraquinone-2-sulphonate, which is red when reduced by zinc amalgam and colourless when oxidised by O present in the sample of gas. The reagent circulates in the apparatus (described and illustrated) in a closed circuit, reacting with the gas and then being regenerated in a reducing column. The intensity of the colour of the reagent is proportional to the amount of O. The percentage of O in the sample is determined by bringing a second portion of the reagent to the same colour by treatment with a sample of gas containing a known proportion of O. The apparatus permits the determination of O in the range 0 to 0·1% by vol., but can be adapted to measure quantities $<$0·01%. The time required for a determination is $\simeq$30 min. and the quantity of gas required is 2 litres.

**III. Continuous determination of small quantities of chlorine in gases.** S. Waszak. *Ibid.*, 1959, **4** (1–2), 351–359.—The apparatus (described and illustrated) is designed for the continuous visual colorimetric determination of small amounts of Cl (up to 0·010%, or up to 0·001% by vol. with an accuracy of $\pm$10%). The method makes use of the reaction of Cl with an aq. soln. of KI, buffered to pH 7, according to the equation $2KI + Cl_2 = I_2 + 2KCl$. The liberated iodine colours the reagent yellow, the variations in intensity being measured by a differential photometer, and recorded on a calibrated automatic recorder. Oxidising substances that produce similar reactions with KI (*e.g.*, $NO_2$) must be removed from the sample before examination. W. B. MIASKOWSKI

5053. **Automation in analytical chemistry. II. Apparatus for serial determinations of enzyme activity.** B. Večerek, K. Kácl, L. Kolařík, B. Chundela and J. Večerková (I Inst. Med. Chem., Charles' Univ., Prague). *Chem. Listy*, 1959, **53** (3), 279–280.—A new apparatus is described which enables the colorimetric determination of phosphatases to be carried out automatically. Sodium phenolphthalein phosphate is used as the substrate and the phenolphthalein formed during the course of the reaction is determined colorimetrically in an alkaline medium. The basic part of the described apparatus is constructed from a test-tube transporter by means of which the addition of test soln., buffer and substrate, heating in the thermostat, the addition of the detecting reagent and the measurement of the colour are made automatically.
J. ZÝKA

## Thermal

5054. **Burner with revolving grid.** P. Berthollet. *Chim. Anal.*, 1959, **41** (2), 63–64.—The butane burner described and illustrated permits the simultaneous fusion of 33 specimens without temperature variations. It is compact, the flame is small and gas consumption is reasonable. The apparatus was designed for the preparation of fluoride discs in the fluorimetric determination of U. Results obtained are compared with those given by the type of burner normally in use.
S. M. MARSH

5055. **Recording calorimeter.** J. Pinkava and Z. Večeřa (School of Chem. Technol., Prague). *Chem. Průmysl*, 1959, **9** (3), 135–137.—A new type of calorimeter, which permits the automatic registration of temp. changes, is based on a combination of a Wheatstone bridge with the Kohlrausch drum of a polarograph. The current intensity is measured by means of the galvanometer and is registered photographically. The calorimeter is a Dewar vessel with device for breaking the ampoules containing the sample. The sensitivity of the described

apparatus is higher than that of a Beckmann thermometer and can be used for the registration of changes of 0·001°. J. ZÝKA

5056. **Torsion thermobalance.** [I]. J. Cueilleron and O. Hartmanshenn (Fac. des Sci., 93 rue Pasteur, Lyons, France). *Bull. Soc. Chim. France*, 1959, **26** (1), 164–168.—A thermobalance is described in which a torsion wire, provided with a beam carrying a counterweight and a pan hanging down into an electric furnace, is mounted in a Pyrex-glass enclosure which can be evacuated. Automatic recording is effected by fitting a shutter to the suspension wire so that it half obscures a photo-electric cell mounted outside the vacuum enclosure. The current from the cell is amplified and fed to a galvanometer with two contacts, which switch on a reversible slow motor (1 rev. per hr.) which twists the torsion head until the shutter is again in the equilibrium position. A pulley on the torsion head connects with the recorder pen. By varying the nature of the torsion wire (0·25-mm-diam. steel piano-wire, 0·15-mm Swedish steel, 0·45-mm or 0·25-mm Elinvar) and the diam. of the pulley, loads from 1 to 15 g can be handled and changes of from 1 to 300 mg can be recorded. The standardisation, use, avoidance of hunting, and theory of the balance are discussed.

**II. Application to the decomposition under vacuum of some sulphates.** J. Cueilleron and O. Hartmanshenn. *Ibid.*, 1959, **26** (1), 168–172.—The decomposition of a number of sulphates was investigated under continuous pumping in the thermobalance described above. Under these conditions the ordinary hydrates of $CuSO_4$, $CaSO_4$, $CoSO_4$, $NiSO_4$, $MgSO_4$, $ZnSO_4$, $CdSO_4$ and $MnSO_4$, and anhyd. $Fe_2(SO_4)_3$, $CdSO_4$, $SnSO_4$ and $Sn(SO_4)_2$, dehydrate without the formation of a basic salt (except with Zn and Cd) and then (except for Ca) decompose at higher temp. to the oxides which are stable at their temp. of formation (except for CdO which decomposes to Cd and O). At high temp. NiO and CoO undergo a partial loss of O to give a ferromagnetic substance; $CaSO_4$ remains stable up to 970°. Some complex sulphates and alums were also studied under continuous pumping and it was found that $Cr_2(SO_4)_3.18H_2O$ loses $9H_2O$ at room temp., then is dehydrated and begins to decompose to oxide at 150°; $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$ loses $6H_2O$ at 90°, gives the anhyd. salt and then decomposes to $Fe_2(SO_4)_3$ and then to $Fe_2O_3$, while $Cr_2(SO_4)_3.K_2SO_4.24H_2O$ loses $6H_2O$ at room temp. and the anhyd. salt (stable from 100° to 400°) decomposes to $Cr_2O_3.K_2SO_4$. A method of quant. analysis of mixtures of sulphates is indicated in which Mg, Mn and Ca individually, or Mg and Mn together, in iron, could thus be determined with an accuracy of 1%.

**III. Application to the decomposition under vacuum of some chlorides.** J. Cueilleron and O. Hartmanshenn. *Ibid.*, 1959, **26** (1), 172–176.—The thermal decomposition of Recoura's green salt $[CrCl_2(H_2O)_4]Cl.2H_2O$ and violet salt $[Cr(H_2O)_6]Cl_3$ and of $SnCl_2.2H_2O$ has been studied by means of the torsion thermobalance. E. J. H. BIRCH

5057. **Simple method for derivative differential thermal analysis.** E. S. Freeman and D. Edelman (Pyrotechnics Chem. Res. Lab., Picatinny Arsenal, Dover, N.J., U.S.A.). *Anal. Chem.*, 1959, **31** (4, Part I), 624–625.—The method described involves using a duplicate sample as the reference material and maintaining a constant temp. differential in the applied temp. between both samples. Conventional differential thermal analysis apparatus is used. The theoretical basis of the method is discussed. K. A. PROCTOR

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*See also Abstract*—**5063**, Differential potentiometer for measuring changes of temp.

## Electrical

5058. **Construction of thread-type salt bridge and immersion-type silver - silver chloride electrode.** J. T. Stock (Dept. of Chem., Univ. of Connecticut, Storrs, U.S.A.). *Chemist Analyst*, 1959, **48** (1), 8–9.—A thread-type salt bridge is constructed by drawing 6-mm glass tubing down to a bore of 1 mm. When cooled just to softening-point, an asbestos thread, 10 mm × 0·5 mm (which has been soaked in HCl, washed and thoroughly dried), is inserted so that 3 mm projects. Keeping the projecting thread as cool as possible, heat is re-applied till the tube collapses on the thread, when the end of the tube is momentarily pinched with a pair of pliers so that the end is flattened for about 3 mm, and the end of the asbestos thread is nipped off flush with the end of the tube. Only enough force to well flatten the tube should be used. With practice, fair reproducibility can be achieved, moderate pinching giving a resistance of 3000 to 5000 ohms and a leak rate, under a 10-cm head, of 0·03 to 0·05 ml per hr. Harder pinching increases the resistance and decreases the leak-rate by a factor of about 5. The construction of a silver - silver chloride electrode embodying such a salt bridge is described and illustrated. R. E. ESSERY

5059. **Electrochemical separation process for use in polarography.** R. L. Faircloth (Res. Group, A.E.R.E., Harwell, Berks., England). *Talanta*, 1959, **2** (2), 135–151.—If pure bismuth is dissolved in mercury and the amalgam placed in contact with *M* HCl containing $Bi^{3+}$, the amalgam takes up a potential controlled by the relative concn. of Bi in the amalgam and $Bi^{3+}$ in the aq. phase, and this potential is little affected by trace impurities in the bismuth. If the standard potential of the electrode reaction $M(Hg) = M^{n+} + nE$, where M is a metallic impurity, is more negative than the actual amalgam potential, the metal M tends to pass into the aq. phase, which can then be examined polarographically. The concn. of $Bi^{3+}$ in the aq. phase can be controlled by adding a known amount of HgCl to the soln., whereby $Hg^+$ are reduced to the metal, and an equiv. amount of Bi passes into the soln. For the determination of impurities in bismuth, mercury (10 ml) is placed in a glass tube and covered with 2 ml of *M* HCl containing 0·4% of HgCl. Bismuth in small pieces (1 g) is dropped into the tube, the air is displaced by N, and the tube is stoppered and gently shaken, with warming, till the bismuth has dissolved. After further vigorous shaking for 15 min., a known vol. of the aq. phase is examined in a square-wave polarograph in the usual way. The accuracy is ±2%. The conditions for the 99·5% extraction of the impurities from the bismuth are discussed with reference to the Nernst equation, and it is shown that Cd, In, Pb, Tl and Zn can be estimated, but not Cu. Other determinations referred to are of Zn in cadmium and of trace impurities in salt soln. The method can be applied to other metals which are sol. in mercury, and it is also suitable for conventional d.c. polarography. R. E. ESSERY

5060. **Rotating sample table for multiple polarographic analyses.** J. Luck (Minneapolis-Honeywell Regulator Co., Minneapolis, Minn., U.S.A.). *Chemist Analyst*, 1959, **48** (1), 18.—The apparatus (illustrated) consists of three metal discs (the upper two bored with holes to carry the sample tubes), mounted one above the other on a hollow central shaft, which rotates on a bearing near its top. The shaft is fitted with radial tubes, to carry nitrogen through rubber tubes to the bubblers inserted in the samples. The reference and dropping mercury electrodes are mounted on a stand as a separate unit. The table is rotated to bring each sample tube in turn into position, the bubbler being then lifted from the sample tube, the electrode assembly inserted, and the polarogram recorded.
R. E. ESSERY

5061. **Determination of low concentrations by the method of differential [subtractive] oscillographic polarography.** Yu. M. Kargin (Kazan State Univ.). *Zavod. Lab.*, 1959, **25** (3), 273–276.—Concn. of Cd, Pb, Bi and Zn of $\simeq 10^{-6}$ *M* are determined by the use of two, not identical, dropping mercury electrodes, the dropping times of which are synchronised by means of saw-tooth impulses. A wiring diagram of the apparatus is given.
G. S. SMITH

5062. **Use of potential compensators in polarographic titrations.** L. Klír, K. Liška and Z. Tischer (Inst. Res. Ores, Prague). *Chem. Listy*, 1959, **53** (4), 432–433.—A new device has been suggested for polarographic titrations for use with a rotating platinum electrode and a S.C.E. A resistance is switched into the circuit instead of the galvanometer and the resulting potential is measured with a potential compensator. The method has been tested on the titration of $As^{3+}$ (0·0001 *N*) with $KBrO_3$.
J. ZÝKA

5063. **An electronic recording differential potentiometer.** C. Solomons and G. J. Janz (Dept. of Chem., Rensselaer Polytech. Inst., Troy, N.Y., U.S.A.). *Anal. Chem.*, 1959, **31** (4, Part I), 623.—The equipment described has been used to record cooling curves during cryoscopic experiments on molten salt soln. in the temp. range 200° to 400°. Temperatures may be read off the recorder chart to the nearest 0·01°. The final 3° of the cooling curve is spread over 4 inches of chart. In measuring the rise in temp. of a calorimeter when determining the heats of fusion of organic salts, temp. changes of $\simeq 1°$ can be readily measured to within 0·005°.
K. A. PROCTOR

5064. **Electronic controlled-potential coulometric titrator. I.** M. T. Kelley, H. C. Jones and D. J. Fisher (Oak Ridge National Lab., Tenn., U.S.A.). *Anal. Chem.*, 1959, **31** (4, Part I), 488–491.—The titrator can be used for either oxidation or reduction coulometric titrations with good precision and can be used either automatically or manually.

**II.** M. T. Kelley, H. C. Jones and D. J. Fisher. *Ibid.*, 1959, **31** (5), 956.—Circuit changes have been made to improve the performance of the electronic controlled-potential coulometric titrator described in Part I.
K. A. PROCTOR

5065. **Use of molecular filter membrane in mounting and assaying of radioactive precipitates.** R. E. Jervis (Chem. and Met. Div., Atomic Energy of Canada Ltd., Chalk River, Ontario). *Talanta*, 1959, **2** (1), 89–91.—Molecular filter membrane has a much lower weight per unit area than filter-paper and undergoes no detectable loss in weight when heated for 30 min. at 120°. It is more suitable than filter-paper for assaying radioactive ppt., but must be used with care since it has a lower mechanical strength and is soluble in some organic solvents. A machined Teflon filtration apparatus for use with molecular filter membranes is illustrated.
W. T. CARTER

5066. **Photomultiplier window for a liquid scintillator.** R. M. Tennent (Univ. of Leeds, England). *J. Sci. Instrum.*, 1959, **36** (3), 148.—The glass of a 2·5-in. cylindrical glass - metal seal is cut 0·75 in. from the seal and a flat glass plate sealed to the end. The metal is soft-soldered directly to the stainless steel of the scintillator tank. The exposed portion of the metal (Kovar) tube and the solder joint are painted with a mixture of titanium oxide and water-glass to avoid the risk of poisoning the scintillator.
G. SKIRROW

5067. **Precision calibration of large $4\pi$ scintillation crystals for routine $\gamma$-counting.** L. J. Colby, jun., and J. W. Cobble (Dept. of Chem., Purdue Univ., Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 798–799.—A large well-type scintillation crystal counter is calibrated by the $4\pi$ $\beta$-$\gamma$ coincidence method and can then be used as a secondary standard for calibrating electron-capture isotopes with a much higher accuracy ($\pm$ 3%) than was previously possible. The system is applicable to the analysis of mixed isotopes and of decay schemes.
K. A. PROCTOR

5068. **Absolute $\beta$ standardisation using $4\pi$ $\beta$-$\gamma$ coincidence techniques.** R. Gunnink, L. J. Colby, jun., and J. W. Cobble (Dept. of Chem., Purdue Univ., Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 796–798.—The use of the $4\pi$ $\beta$-$\gamma$ coincidence counter is recommended as a primary $\beta$-standardising method as it is free from many disadvantages but requires a true $\beta$-$\gamma$ coincidence. The $4\pi$ method can be evaluated against this procedure.
K. A. PROCTOR

5069. **Evaluation of the Cenco $\beta$-ray H/C meter. A new calibration procedure.** R. Rowan, jun. (Products Res. Div., Esso Res. and Engng Co., Linden, N.J., U.S.A.). *Anal. Chem.*, 1958, **31** (4, Part I), 558–561.—A new method of determining the fundamental instrument constant, $K_H$, is described. The precision lies in the range of 0·01 to 0·02% of H for pure or mixed hydrocarbon samples. The accuracy depends on the exactness of the calibration.
K. A. PROCTOR

5070. **Direct estimation of $\gamma$-ray abundances in radionuclide mixtures. Complement subtraction method.** W. Lee (U.S. Naval Radiolog. Defense Lab., San Francisco, Calif., U.S.A.). *Anal. Chem.*, 1959, **31** (5), 800–806.—$\gamma$-Emitting radionuclides can be determined in mixtures by a direct rapid technique which combines the use of an Argonne-type 256-channel pulse-height analyser with a dead-time correcting device. Pure calibrated standards are required for each radionuclide and this limits the accuracy of the method for absolute quant. work.
K. A. PROCTOR

5071. **Sensitivity charts for neutron activation analysis.** W. W. Meinke (Univ. of Michigan, Ann Arbor, U.S.A.). *Anal. Chem.*, 1959, **31** (5), 792–795.—Sensitivity charts are given for a number of elements irradiated by thermal neutrons for periods of 6 min., 10 hr. and 1000 hr., and are useful for comparing the sensitivities of this and other methods of analysis. K. A. PROCTOR

5072. **Chemical analysis by neutron activation.** J. Fouarge (Lab. Chim. Anal., Univ. Liége, Belgium). *Ind. Chim. Belge*, 1959, **24** (2), 143–154.—The theory and limitations of the method, which is sensitive enough for the detection of most elements in the $10^{-5}$ to $10^{-15}$-g range, are discussed, and applications are briefly reviewed. A table of sensitivities is included. (75 references.)
S.C.I. ABSTR.

5073. **An alarm for the detection of toxic industrial gases.** A. M. Kinnear (Chem. Defence Expt. Estab., Porton Down, Salisbury, Wilts., England). *Chem. & Ind.*, 1959, (11), 361–363.—The air is drawn through an illuminated area of filter-paper tape and the production of a coloured reaction product reduces the amount of reflected light received by a photocell and so trips the alarm. A built-in reagent pump can be used to impregnate the paper with up to three separate reagents or, alternatively, a dry, untreated or previously impregnated tape may be used. Approx. limits of detection are 0·3 p.p.m. of $H_2S$, 0·5 p.p.m. of HCN, 0·9 p.p.m. of $COCl_2$, 0·1 p.p.m. of Cl and 1·5 p.p.m. of $SO_2$. K. A. PROCTOR

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*See also Abstracts*—**4983**, Portable analyser for dissolved O in water. **4991**, Automatic titrator for sewage.

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ERRATA

July (1958) issue, abstract 2272, line 10. *For* "Kircha" *read* "Kirchner."

January (1959) issue, abstract 283, line 2. *For* "Rathbon" *read* "Rathbun."

March (1959) issue, abstract 1006, line 4. *For* "Kirsh" *read* "Kirsch."

April (1959) issue, abstract 1175, last line in second column. *For* "Rease" *read* "Reese."

April (1959) issue, abstract 1285, lines 1 and 5. *For* "chronometric" *read* "chromometric."

July (1959) issue, abstract 2621, line 5. *For* "Bi" *read* "Pd."

July (1959) issue, abstract 2662, line 12. *For* "metal" *read* "metol."

August (1959) issue, abstract 2847, last line. *For* "$KCrO_4$" *read* "$K_2CrO_4$."

August (1959) issue, abstract 2857, line 5. *For* "2008" *read* "2808."

August (1959) issue, abstract 2943, line 13. *For* "1-(2-pyridyl)azo.1-2-naphthol" *read* "1-(2-pyridyl)azo-2-naphthol."

August (1959) issue, abstract 3073, line 4. *For* "1958" *read* "1959."

September (1959) issue, abstract 3374, line 7. *For* "$Na_3H_2IO_6$" *read* "$Na_2H_3IO_6$."

October (1959) issue, abstract 4196, line 1. *For* "dimeton-methyl" *read* "demeton-methyl."

# ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

| | |
|---|---|
| alternating current | a.c. |
| ampere | amp. |
| Ångström unit | A |
| anhydrous | anhyd. |
| approximate, -ly | approx. |
| aqueous | aq. |
| atmospher-e, -ic | atm. |
| boiling-point | b.p. |
| British thermal unit | B.Th.U. |
| calorie (large) | kg-cal. |
| calorie (small) | g-cal. |
| centimetre | cm |
| coefficient | coeff. |
| concentrated | conc. |
| concentration | concn. |
| constant | const. |
| corrected | (corr.) |
| crystalline / crystallised | cryst. |
| cubic | cu. |
| current density | c.d. |
| cycles per second | c/s |
| density | $\rho$ |
| density, relative | $d$ or wt. per ml |
| dilute | dil. |
| direct current | d.c. |
| distilled | dist. |
| ethylenediaminetetra-acetic acid | EDTA |
| electromotive force | e.m.f. |
| equivalent | equiv. |
| gram | g |
| gram-molecule | mole |
| half-wave potential | $E_{\frac{1}{2}}$ |
| hour | hr. |
| hydrogen ion exponent | pH |
| infra-red | i.r. |
| insoluble | insol. |
| international unit | i.u. |
| kilogram | kg |
| kilovolt | kV |
| kilowatt | kW |
| liquid | liq. |
| maxim-um, -a | max. |
| melting-point | m.p. |
| microgram | $\mu$g (not $\gamma$) |
| microlitre | $\mu$l |
| micromole | $\mu$mole |
| micron | $\mu$ |
| milliampere | mA |
| milli-equivalent | milli-equiv. |
| milligram | mg |
| millilitre | ml |
| millimetre | mm |
| millimicrogram | m$\mu$g |
| millimolar | m$M$ |
| millivolt | mV |
| minute (time) | min. |
| molar (concentration) | $M$ |
| molecul-e, -ar | mol. |
| normal (concentration) | $N$ |
| optical rotation | $\alpha_\lambda^t$ |
| ounce | oz |
| parts per million | p.p.m. |
| per cent. | % |
| per cent. (vol. in vol.) | % (v/v) |
| per cent. (wt. in vol.) | % (w/v) |
| per cent. (wt. in wt.) | % (w/w) |
| potential difference | p.d. |
| precipitate (as a noun) | ppt. |
| precipitated | pptd. |
| precipitating | pptg. |
| precipitation | pptn. |
| preparation | prep. |
| qualitative, -ly | qual. |
| quantitative, -ly | quant. |
| recrystallised | recryst. |
| refractive index | $n_D^t$ |
| relative band speed | $R_F$ |
| relative humidity | r.h. |
| revolutions per minute | r.p.m. |
| saponification value | sap. val. |
| saturated calomel electrode | S.C.E. |
| second (time) | sec. |
| soluble | sol. |
| solution | soln. |
| specific gravity | sp. gr. |
| specific rotation | $[\alpha]_\lambda^t$ |
| square centimetre | sq. cm. |
| standard temp. and pressure | s.t.p. |
| temperature | temp. |
| ultra-violet | u.v. |
| vapour density | v.d. |
| vapour pressure | v.p. |
| volt | V |
| volume | vol. |
| watt | W |
| wavelength | $\lambda$ |
| weight | wt. |

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

| | | | |
|---|---|---|---|
| greater than | $>$ | less than | $<$ |
| not greater than | $\ngtr$ | not less than | $\nless$ |
| is proportional to | $\propto$ | of the order of, approximately | $\simeq$ |

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, $Fe^{II}$, $Mo^{V}$. Substances in the ionic state are represented by $Na^+$, $Fe^{2+}$, $Fe^{3+}$, etc., for cations and by $Cl^-$, $SO_4^{2-}$, $PO_4^{3-}$, etc., for anions.

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# ANALYTICAL ABSTRACTS

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